



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B32B 7/12, 15/08, C08K 5/521 C09J 125/14, 133/02, 133/08 C09J 133/10, 133/26	A1	(11) International Publication Number: WO 91/18739 (43) International Publication Date: 12 December 1991 (12.12.91)
(21) International Application Number: PCT/US91/03750 (22) International Filing Date: 24 May 1991 (24.05.91) (30) Priority data: 530,013 29 May 1990 (29.05.90) US (71) Applicant: ASHLAND OIL, INC. [US/US]; P.O. Box 2219, Columbus, OH 43216 (US). (72) Inventor: SKOGLUND, Michael, Jeffrey ; 5728 Tara Hill Drive, Dublin, OH 43017 (US). (74) Agents: PICKEN, Mary, E.; Ashland Chemical Company, P.O. Box 2219, Columbus, OH 43216 (US) et al.		(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>
(54) Title: WATER-BORNE ACRYLIC EMULSION PRESSURE SENSITIVE LATEX ADHESIVE COMPOSITION (57) Abstract <p>The present invention is directed to an aqueous emulsion acrylic pressure sensitive adhesive composition that excels in high performance applications. The inventive adhesive composition comprises in water (a) a copolymer of a C₄-C₁₈ alkyl (meth)acrylate monomer and between about 0.1 % and 5 % N-substituted or unsubstituted (poly)acrylamide; (b) a copolymer of a C₄-C₁₈ alkyl (meth)acrylate monomer and between about 0.2 % and 10 % of an ethylenically-unsaturated carboxylic acid; and (c) a surfactant, which preferably comprises between about 0.01 % and 10 % by dry weight of said copolymers of a phosphate ester surfactant. Said copolymers (a) and (b) are selected from: (i) a blend of copolymers (a) and (b), at least one of which is an emulsion copolymer; (ii) an interpolymers of copolymers (a) and (b) where said alkyl (meth)acrylate monomer of copolymers (a) and (b) are the same; and (iii) an interpenetrating polymer network of copolymers (a) and (b). Advantageously, the ratio of acrylamide to unsaturated acid in the copolymer ranges from about 1:10 to 10:1 by weight. Advantageously, the emulsion copolymer(s) includes up to 25 % by weight of styrene or other aromatic monomer(s).</p> <div style="text-align: right; margin-top: 200px;"><i>103 Ref</i></div>		

Printed by EAST

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Computer: TRN03389

Date: 10/04/2007

Time: 13:51

Document Listing

Document	Image pages	Text pages	Error pages
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Total	77	0	0

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WATER-BORNE ACRYLIC EMULSION PRESSURE SENSITIVE LATEX ADHESIVE COMPOSITION

Cross-Reference to Related Applications

This application is a continuation-in-part of application USSN 07/530,013, filed May 29, 1990, the disclosure of which is expressly incorporated herein by
5 reference.

Background of the Invention

The present invention relates to pressure sensitive adhesives and more particularly to a water-based pressure sensitive adhesive suitable for high
10 performance applications.

The manufacture of pressure sensitive adhesive tapes is being shifted from organic solvent systems to aqueous latices in order to reduce air pollution and fire hazard, as well as eliminate the rising expense of organic solvents. Pressure sensitive adhesives for high performance application must meet or exceed diverse,
15 often seemingly incompatible, criteria. Initially, the adhesive must coat well on silicone or other release sheets. The adhesive also must exhibit tenacious adherence to film face stock which may serve a masking function or may convey information, e.g. by its imprinting.

When the adhesive coated film face stock is removed from the release sheet,
20 the adhesive must exhibit initial tack and peel performance when pressure-applied to a substrate. The substrate bearing the adhesively-bound film face stock may be subjected to a variety of manufacturing operations over time. Thermal cycling of the substrate is a condition to which high performance, pressure sensitive adhesives must be designed to confront. When the film face stock is removed from the
25 substrate, removal must be clean, i.e. no visible trace of the adhesive should remain on the substrate. Heat aging of the film face stock/substrate laminate, however, tends to cause the adhesive to "build", that is, the necessity to utilize excessive force to remove the film face stock. Thus, the adhesive should stick well initially, but not so well that its later removal is difficult. Then too, the adhesive must possess shelf
30 life, viscosity, etc. making it compatible with existing coating and handling techniques utilized in the art.

Prior proposals aimed at making pressure sensitive adhesives tapes include, for example, U.S. Pat. No. 3,657,396 which proposes a mixture of polyvinylmethyl ether and an acrylic acid polymer which mixture is dispersed in
35 water. The acrylic polymer is selected from the group consisting of polyacrylic

acid, polyacrylamide, N-methylol polyacrylamide and an acrylic copolymer of a monomer selected from the group consisting of acrylic acid, acrylamide, and N-methylol acrylamide in a monomer selected from the group consisting of lower alkyl esters of acrylic acid and methacrylic acid. European patent application
5 publication No. 287306 proposes removable pressure-sensitive adhesive tapes comprising copolymers of terminally-unsaturated vinyl monomers and vinyl-unsaturated homopolymerizable emulsifier monomers, combined with a phosphate emulsifier. Japanese Kokai patent No. Sho 47 [1972]-110263 proposes a transfer-resistant aqueous pressure sensitive adhesive comprising a resin emulsion derived
10 from an acrylic monomer and 1-4 weight parts of an ethylenically-unsaturated acrylamide monomer. Australian application No. 24491/84 proposes pressure sensitive adhesives comprising an acrylic copolymer synthesized from 2-ethylhexyl acrylate and n-butyl acrylate, acrylonitrile, acrylic acid, N-methylol acrylamide, and optionally vinyl sulfonic acid; and plasticizer.

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Broad Statement of the Invention

The present invention is directed to an aqueous emulsion acrylic pressure sensitive adhesive composition that excels in high performance applications. The inventive adhesive composition comprises in water (a) a copolymer of a C₄-C₁₈
20 alkyl (meth)acrylate monomer and between about 0.1% and 5% N-substituted or unsubstituted (poly)acrylamide; (b) a copolymer of a C₄-C₁₈ alkyl (meth)acrylate monomer and between about 0.2% and 10% of an ethylenically-unsaturated carboxylic acid; and (c) a surfactant, which preferably comprises between about 0.01% and 10% by dry weight of said copolymers of a phosphate ester surfactant.
25 Said copolymers (a) and (b) are selected from: (i) a blend of copolymers (a) and (b), at least one of which is an emulsion copolymer; (ii) an interpolymer of copolymers (a) and (b) where said alkyl (meth)acrylate monomer of copolymers (a) and (b) are the same; and (iii) an interpenetrating polymer network of copolymers (a) and (b). Advantageously, the ratio of acrylamide to unsaturated acid in the
30 copolymer ranges from about 1:10 to 10:1 by weight. Advantageously, the emulsion copolymer(s) includes up to 25% by weight of styrene or other aromatic monomer(s).

In high performance applications, the novel adhesive composition is substantially-free of cross-linking monomers, copolymerizable emulsifiers, N-methylol acrylamides and the like, cross-linking additives (*i.e.* post-polymerization
35 addition yielding a cross-linking reaction or formation of interpolymer bonds, such as, for example, zinc salts, diisocyanates, diglycidyl compounds, *etc.*), and zwitterionic monomers (*i.e.* not more than about 15 wt-% of cross-linking

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ingredient, including monomers and additives). Basification of the copolymer(s) results in a self-thickening adhesive composition and contributes to manufacturing reproducibility of the adhesive composition.

Advantages of the present invention include a manufacturing process that enables the reproducible production of the novel adhesive composition. Another advantage is the ability to synthesize an adhesive composition base that is compatible and blendable with other conventional ingredients at all levels. A further advantage is the ability to produce an ultra-removable adhesive composition. These and other advantages will be readily apparent based upon the disclosure set forth herein.

Detailed Description of the Invention

The major ingredient in the emulsion copolymer(s) broadly is a C₄-C₁₈ alkyl (meth)acrylate monomer and advantageously a C₄-C₁₂ alkyl (meth)acrylate monomer. n-Butyl acrylate and 2-ethylhexyl acrylate are two monomers that have proven advantageous in forming the emulsion copolymer(s) of the present invention, though other straight chain, alicyclic, and cyclic alkyl (meth)acrylate monomers may be used as is necessary, desirable, or convenient. By convention, the parentheticals used herein designate optional content, *i.e.* (meth)acrylate means "acrylate" or "methacrylate", and the same is true for the parenthetical plurals used herein. Also by convention, copolymer and interpolymer both mean a polymer of two or more monomers. The selection of the terms as used herein is for the clarity of understanding and not by way of limitation.

A combination of acrylamide and ethylenically unsaturated carboxylic acid form the balance of the emulsion copolymer(s) and their combination is important to the high performance properties realized, whether present in a single interpolymer or present separately in two different copolymers. The proportion of acrylamide ranges from about 0.1 wt-% to about 5 wt-% while the proportion of unsaturated acid ranges from about 0.2 to about 10% by weight. For present purposes, the acrylamide content includes N-alkyl and other substituted acrylamides and polyamides, *e.g.* diamides. Cross-linking monomers, *e.g.* N-methylol acrylamides, may be present in minor amount (*e.g.* not more than about 15 wt-%), though such latent cross-linking functionality tends to lower tack and initial peel values, thus reducing the strength and suitability of the adhesive composition for some applications. N-methylol substituted acrylamides may be present in the formulation, but they generate formaldehyde when the films are coated which is a health concern in the industry. Latent cross-linking functionality additionally can cause a loss of adhesive properties aged unapplied films and labels. Additive cross-

linkers cause problems is use with adhesive batch-to-batch consistency, pot life, reactivity, and variation in adhesive performance. Fortunately, latent cross-linking functionality and additive cross-linkers are not required of the novel adhesive composition.

5 While the preferred acid simply is acrylic acid, a variety of additional ethylenically unsaturated carboxylic acids may be useful in forming the emulsion copolymer. Additional acids include, for example, butenic acids, *e.g.* crotonic acid, isocrotonic acid, and vinyl acetic acid; an acid from the fumaric acid series, *e.g.* fumaric acid, maleic acid, glutaconic acid, allyl malonic acid, and allyl succinic acid; and dicarboxylic acids, *e.g.* itaconic acid. Lower alkyl-substituted (*e.g.* C₁-C₄ alkyl group) acrylic acid, *e.g.* methacrylic acid, additionally can find use in formulating the emulsion copolymer(s) of the present invention. With respect to the ratio of acrylamide to acrylic acid, such ratio broadly ranges from about 1:10 to about 10:1 by weight with about 1:2 being optimum for acrylamide to acrylic acid. 10:1 by weight with about 1:2 being optimum for acrylamide to acrylic acid. 15 This ratio is believed to be important in providing removability characteristics with retention of good initial tack and peel values.

Optionally, the emulsion copolymers(s) or interpolymer can contain styrene or another aromatic polymerizable monomer, vinyl chloride, vinylidene chloride, ethylene vinyl acetate, or other hydrophobic monomer. Styrene can be present in an amount up to about 25% by weight and preferably about 5% by weight styrene is included in the monomer mixture that is subjected to emulsion copolymerization. 20 in accordance with the precepts of the present invention.

If a single interpolymer of alkyl (meth)acrylate, acrylamide content, and unsaturated acid is used in formulating the novel adhesive composition, then such interpolymer is made by emulsion polymerization techniques. If a blend of copolymers with separate acrylamide and unsaturated acid is used in formulating the novel adhesive composition, then at least one of the copolymers is made by emulsion polymerization techniques, while the other copolymer can be made by emulsion polymerization, solution polymerization, bulk polymerization, suspension polymerization, or other technique [see generally, D.H. Solomon, *The Chemistry of Organic Film Formers*, Robert E. Krieger Publishing Company, Huntington, New York (1977)]. The interpenetrating polymer network can be based either on the acrylamide-containing copolymer or on the unsaturated acid-containing copolymer, though synthesis again is by emulsion polymerization. Details on synthesis of interpenetrating polymer network emulsions can be found in U.S. Patent No. 4,616,057, the disclosure of which is expressly incorporated herein by reference. 25 30 35

The emulsion copolymer(s) or interpolymer can be made by a batch, semi-

batch or continuous process, though preferably a semi-batch process is employed. Despite the ability to meter a constant mixture of the monomers to the reaction vessel, the product emulsion copolymer evidences a two-stage morphology, as will be explored further below. Emulsion polymerization in the aqueous continuous phase is conducted in conventional fashion, such as described by D.H. Solomon in *The Chemistry of Organic Film Formers*, pp 294-303, *supra*.. To this end, a conventional emulsifier, *e.g.* sodium alkylaryl polyethoxy sulfonate or the like, is utilized during the emulsion polymerization reaction. Conventional emulsion polymerization conditions are utilized, though higher non-volatile solids product content may optimize performance, *e.g.* about 50-65% non-volatile solids of the product emulsion copolymer. The reaction is continued until desirably virtually no acrylamide or other unreacted monomer remains. Any residual unreacted monomer should be removed at the end of the reaction in order that its presence does not degrade performance of the novel adhesive composition. Conventional free radical initiators are used, *e.g.* hydrogen peroxide, sodium persulfate, potassium persulfate, ammonium persulfate, and like peroxide and persulfate initiators. Conventional reducing agents (*e.g.* sodium metabisulfate or sodium formaldehyde sulfoxylate) are used as part of the redox catalyst systems. The polymerization preferably is run without a buffer at a pH of about 2-3 as determined by the decomposition of the persulfate catalyst (*i.e.* sulfonic acid generation). Since the pKa of acrylic acid is about 4, the pH of the emulsion reaction mixture should be very low, *e.g.* much less than 4, so that the acrylic acid copolymer does not ionize and thicken during the reaction. Once the reaction is complete, the copolymer can be basified (*i.e.* the pH raised with base above pH of reaction) to a pH of above 3, broadly 3-10, and preferably about 8-9. Basification provides a self-thickening adhesive composition and has been determined to enable manufacturing reproducibility of the adhesive composition. For efficiency and economy, aqueous ammonia can be used to basify the composition, though other bases, *e.g.* various amines, imines, alkali metal and alkaline earth metal hydroxides, carbonates, etc., can be used as is necessary, desirable, or convenient.

In making the emulsion copolymer(s) or interpolymer, it is a distinct advantage that the emulsion copolymer(s) or interpolymer need not contain any cross-linking monomers, copolymerizable emulsifiers, N-methylol acrylamides, or zwitterionic monomers. These ingredients generally lower tack and initial peel values, thus reducing the strength and suitability of the adhesive contact, especially in high performance applications. Latent cross-linking functionality, additionally, can cause a loss of adhesive properties for aged unapplied films and labels and yellowing or discoloration of the adhesive. Thus, while such ingredients can be

included in the emulsion copolymers(s) or interpolymer in minor amount (e.g. not more than about 15 wt-%), they are not necessary and desirably are avoided.

The next ingredient utilized in formulating the novel adhesive composition is a surfactant (preferably a phosphate ester surfactant) that should be present in a proportion of about 0.01% to 10% by dry weight of the emulsion copolymer(s) or interpolymer. The phosphate ester surfactant serves a dual function in the adhesive composition. One function is to promote the removability of a label or other substrate coated with a cured residue of the adhesive composition. The second function is the ability of the phosphate surfactant to wet out silicone release sheets which enhances coatability of such release sheets. Too much phosphate, however, tends to promote foaming of the adhesive composition which detracts from its use in commercial settings. A good discussion of phosphate emulsifiers can be found in European patent application publication No. 287,306, cited above. Examples of these emulsifiers include, for example, ammonium, potassium or sodium salts of alkylaryl polyethoxy phosphates, alkyl ethoxy phosphates, alkyl phosphates, alkyl polyethoxy phosphates, and the like, and even mixtures thereof. The phosphate coester structure augments the removability and other performance characteristics.

The following conceptualizations are proposed to provide a theoretical framework explaining the phosphate coester modified carboxy/amide-containing acrylic emulsion polymer adhesives disclosed herein. While the various polymer-surfactant interactions are supported by known hydrogen bonding in phospholipid chemistry (see Ceve, et al. *Phospholipid Bilayers-Physical Principles and Models*, Wiley-Interscience, John Wiley and Sons), the theory presented below is not a limitation of the present invention.

Carboxyl and amide-containing acrylate polymers may be expected to contain interpolymer hydrogen bond interactions including COOH/CONH₂, COOH/COOH, and CONH₂/CONH₂. These interpolymer associations are believed to contribute to the removable adhesive properties of the novel adhesive composition. Rapid viscosity increases with neutralization of the copolymer indicate a hydrophilic morphology with carboxylate-amide rich polymer segments occurring in the outer layers of the colloid polymer particle. This relationship between polymer structure and performance also is supported by the observation that completion of the reaction at lower non-volatile (nv) solids in combination with consuming unreacting monomers results in a different performance profile for the copolymer. Heat aged performance of different nv solids emulsion copolymer-based adhesive compositions suggest a polymer structure that develops during the polymerization and that this improves adhesive removability. It is believed that polymer hydrophilic morphology develops during the latter states of reaction to

create a carboxylate-amide rich latex shell. This structure is best formed only under specific reaction conditions with specific acid-amide functional ratios.

Typical phosphate coester surfactants contain hydrophobic groups and a -POOH moiety. Commercial synthetic phosphate surfactants are functionally similar to phospholipids and are capable of hydrophobic, hydrogen bonding, and electrostatic interactions. The strong effects observed for blending small amounts of phosphate surfactants on emulsion viscosities and polymer film adhesion performance indicates a strong association between phosphate surfactant and latex particles. The structure of the carboxylate-amide copolymer in combination with the phosphate surfactant also should influence the character of adhesive substrate interfaces. Further, no significant surfactant "bleed" or migration in the phosphate surfactant emulsion has been observed, indicating that the surfactant is absorbed effectively in the colloid polymer film. This is a distinct advantage of the inventive adhesive composition. Prior removable adhesives (*i.e.*, with plasticizers) often bleed through paper face stocks causing disfiguration of the paper label. The inventive adhesive does not "bleed" on paper face stock. This is evidence for attractive interaction and negative free energy of mixing.

Phosphate hydrogen bond or electrostatic interaction is possible with carboxyl and amide polymer groups. Phosphate-polymer associations could form a colloid interpolymer network.

A postulated colloid polymer structure involves an acrylate polymer core surrounded by a carboxyl/amide rich polymer shell. The surface of the latex is composed of the phosphate ester surfactant and the emulsion copolymer emulsifier. The anionic groups of the surfactant and emulsifier support an electrical charged layer around the particle providing colloid stability. Ionization of polymer bound carboxylic acid at, *e.g.*, pH 3-6, expands the outer layers of the latex particle, resulting in increased latex viscosity. Film formation is affected by the outer layer of structure of the colloid polymer during particle coalescence. The structural changes affect film adhesive properties. Polymer film structure is affected by phosphate coester hydrophobe structure and the extent of ionization of the carboxylic functionality. These interfacial phenomena result in specific structural networks in the coalesced latex adhesive film. This film structure, in turn, yields special performance properties (*i.e.* low peel build on aging) having pronounced effects on peel and shear values. Other surfactants (*e.g.* polyoxyethylene-polyoxypropylene block copolymers, alkanol amides, amine oxides, amines, ethoxylated amines, imidazolines, etc.) may be used instead of the preferred phosphate coester surfactants.

With respect to performance of the adhesive composition, advantageously,

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the adhesive is removable from a variety of substrates cleanly, *i.e.* no visible residue, including, for example, metals (*e.g.*, stainless steel, aluminum, *etc.*) and plastics (*e.g.*, polyethylene, polypropylene, polystyrene, polycarbonate, ABS resin, PVC resin, *etc.*) Build on aging generally is less than 100% when the applied adhesive is maintained at 70° C for three weeks and less than 50% when aged at room temperature for three weeks. A viscosity of about 1,000-10,000 centipoises is compatible with existing equipment and handling procedures, and preferably a viscosity of about 2,000-4,000 centipoises is maintained. Consistent with the theory expounded above is that testing has revealed that high surface energy polymeric film face stocks provide outstanding performance to the adhesive composition. Surface energy is the product obtained by multiplying surface tension by the two-thirds of the molecular weight and specific volume (*e.g.* see U.S. Pat. No. 4,529,563). Such face stocks include, for example, plasticized polyvinyl chloride and polyester films. Other film face stocks also are useful including, for example, cellulose, metal foil, composites, and the like. In this regard, an emulsion copolymer based on 2-ethylhexyl acrylate has been determined to retain improved aged adhesive performance on plasticized vinyl facestock.

Conventional additives may be incorporated into the adhesive composition, including, for example, wetting agents, pigments, opacifying agents, anti-foam agents, and the like and mixtures thereof. The adhesives may be applied to one or both sides of the film face stock in a conventional manner, for example, by spraying, knife coating, roller coating, casting, drum coating, dipping, and the like. Indirect application using a transfer process with silicon release paper also can be used. After the adhesive has been applied, the coated film face stock is dried conventionally.

The following examples show how the present invention has been practiced, but should not be construed as limiting. In this application, all percentages and proportions are by weight and all units are in the metric system, unless otherwise expressly indicated. Also, all citations referred to herein are expressly incorporated herein by reference.

IN THE EXAMPLES

The emulsion polymerization procedure used to make the acrylic emulsion copolymers will be illustrated by the following detailed procedure. Material variances from this typical synthesis and the specific monomer mixtures will be detailed in the working examples.

TABLE 1**Emulsion Copolymer 4886-155**

	<u>Ingredient</u>	<u>Amount (wt-parts)</u>
	<u>Monomer Emulsion</u>	
5	Butyl acrylate	740.0
	Styrene	36.0
	Acrylic acid	16.0
	Acrylamide	8.0
	Triton X-200*	72.0
10	DI Water**	196.3
	<u>Catalyst #1</u>	
	Sodium Bisulfite	0.8
	DI Water	8.0
	<u>Catalyst #2</u>	
15	Potassium Persulfate	2.4
	DI Water	46.4
	<u>Catalyst #3</u>	
	t-Butyl Hydroperoxide	0.4
	DI Water	10.0
20	<u>Catalyst #4</u>	
	Sodium Formaldehyde Sulfoxylate	0.2
	DI Water	4.0
	* Triton X-200 emulsifier is sodium alkyl aryl polyethoxy sulfonate, 28 wt-% actives, Union Carbide Corporation, Danbury, CT.	
25	** DI Water is deionized water.	

Emulsion polymerizations were conducted in a 3-liter Pyrex brand glass reactor equipped with water bath, mechanical stirrer, N₂ atmosphere, condenser, thermocouple, and pumps for monomer and initiator feeds. A monomer emulsion was prepared with 800 g total monomer (the amount used in all preparations), deionized water (196.3 g), and Triton X-200 emulsifier. The reactor was charged with deionized water (230 g) and the initial monomer emulsion (21.3 g, 2.0%) and warmed to 76° C initiation temperature with stirring. Catalyst #1 and 2 wt-% of catalyst #2 were used to initiate the reaction.

After the initiation reaction, the remaining monomer emulsion and potassium persulfate solution were delayed fed at a constant rate over a 3 hour time period while maintaining a reaction temperature of 80° C. The reaction temperature was maintained for an additional 30 minutes after the feed ended.

The reaction temperature then was lowered to 50° C and chaser catalysts, *tert*-butyl hydroperoxide (70%) aqueous solution (0.4 g in 10 ml) and sodium formaldehyde sulfoxylate aqueous solution (0.4 g in 10 ml), were added to reduce residual monomer content. The reaction temperature of 50° C was maintained for 30 minutes and then lowered to 35° C, and a biostat (Kathon LX, 1.5%, 2 g) was added. Emulsion copolymer 4886-155 had a solids content of 61%, a pH of 2.6, and viscosity of 3,040 cps (Brookfield RV spindle #4 at 20 rpm).

The following test procedures were used in the examples:

1. 180° Peel Test: PSTC-1 (November 1975), Pressure Sensitive Tape Council, Glenview, Ill. Results of this test are reported in pounds/inch.
2. 178° Shear Test: PSTC-7 (November 1975). Pressure Sensitive Tape Council. Results of this test are reported in hours/1000 gm/0.5 in² at 23°C.
3. Polyken Tack Test: This test is conducted on a Polyken, Jr. Probe Tack Tester (Polyken is a trademark of the Kendall Company) supplied by Testing Machines, Inc. (Amityville, N.Y.) under the following conditions:

20	Probe:	304 SS. 0.5 cm. diameter probe polished to 4/0 emery paper finish.
	Dwell Time:	1 second
	Probe Contact Pressure:	100 gm/cm ²
	Probe Retraction Rate:	1 cm/sec.
25	Annular Weight:	20 gm. - 100 gm/cm ² pressure of a 0.5 cm. diameter probe
30	Procedure:	A one-inch square of MYLAR polyester film coated with the adhesive is placed on top of the annular weight so that the hole is completely covered by the adhesive area and this assembly placed in the weight carrier well. The machine is activated and the sequence of probe pressure and probe retraction automatically accomplished. The force required to free the probe from adhesive coated film, measured in
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grams/cm² is read from the indicator dial on the machine.

EXAMPLE 1

- 5 Emulsion copolymers were synthesized by the typical emulsion polymerization procedure detailed above from the following monomer mixtures.

TABLE 2

10	Copolymer Emulsion	*Monomer (wt-parts)								
	No.	BA	STY	AA	AMD	MSTY	MMA	RSH	DVB	NMA
	4886-116	93.5	4.5	2.0	--	--	--	--	--	--
	4886-118	93.5	4.5	2.0	--	--	--	0.025	--	--
	4886-155	92.5	4.5	2.0	1.0	--	--	--	--	--
15	4886-176	93.5	4.5	1.0	1.0	--	--	--	--	--
	4886-181	92.5	--	2.0	1.0	4.5	--	--	--	--
	4886-183	92.0	4.5	2.0	1.5	--	--	--	--	--
	4886-185	92.3	4.5	2.0	1.0	--	--	--	0.2	--
	4886-187	97.0	--	2.0	1.0	--	--	--	--	--
20	4886-189	92.0	4.5	2.5	1.0	--	--	--	--	--
	4924-4	90.5	6.0	2.5	1.0	--	--	--	--	--
	4924-6	87.5	4.5	2.5	1.0	--	4.5	--	--	--
	4924-30	86.0	4.5	2.5	1.0	--	6.0	--	--	--
	4924-32	84.0	4.5	2.5	1.0	--	8.0	--	--	--
25	4817-193	92.5	5.0	2.0	--	--	--	--	--	0.5

*BA - butyl acrylate

STY - styrene

AA - acrylic acid

AMD - acrylamide

30 MSTY - methyl styrene

MMA - methyl methacrylate

RSH - dodecylmercaptan

DVB - divinyl benzene

NMA - N-methylol acrylamide

- Each of the emulsion copolymers then was neutralized with aqueous ammonia (29 wt-%) and blended with Pluronic L-121 surfactant (polyoxypropylene-polyoxyethylene block polymer, HLB value of 5.0, BASF
35 Wyandotte Chemical Co.), as follows:

TABLE 3

	Adhesive No.	Emulsion Copolymer	Ingredients (wt-parts)		pH
			Aqueous Ammonia (ml)	Pluronic Surfactant	
5	4886-116	450	2.4	5.0	8.2
	4886-118	450	1.4	5.0	7.0
	4886-155	200	*	2.22	--
	4886-176	200	0.8	2.22	8.5
10	4886-181	200	1.2	2.22	8.0
	4886-183	200	1.2	2.22	8.1
	4886-185	200	1.0	2.22	8.0
	4886-187	200	1.0	2.22	8.0
	4886-189	200	1.0	2.22	8.0
15	4924-4	200	1.2	2.22	--
	4924-6	200	1.2	2.22	--
	4924-30	100	*	1 wt-%	--
	4924-32	100	*	1 wt-%	--
	4294-193	100	*	1 wt-%	--
20	* Ammonia added to nominal viscosity of about 2,000 cps.				

Experimental adhesives were transfer coated to Mylar brand film (1 mil dry film thickness), and tests conducted. In all data reported, unparenthesized values are for free films cured for 24 hours at room temperature and constant humidity (50% RH). Parenthesized values are for free films cured for one week at 70° C. "Heat Aged" specimens were heated at 70° C for 24 hours, then equilibrated at room temperature for 24 hours. The following results were recorded:

TABLE 4

Adhesive No.	Polyken Tack (g/cc)	180° Shear (hrs/1000 g/ 0.5 in ²)	180° Peel (pounds/inch)			Heat Aged
			15 min	24 hr		
4886-116	330 (330)	2.8 (5.3)	1.1 (1.2)	1.8 (2.1)		3.1
4886-118	340 (410)	0.7 (0.9)	1.4 (1.5)	2.7 (2.5)		3.1
4886-155	310 (260)	3.3 (3.4)	0.6 (0.4)	0.9 (1.2)		1.8
4886-176	230	4.4	0.7	1.4		2.1
4886-181	150 (280)	1.6 (1.6)	0.6 (0.5)	1.0 (1.5)		1.4
4886-183	160 (230)	1.1 (0.5)	0.6 (0.3)	0.7 (1.0)		1.4
4886-185	190 (370)	0.7 (0.2)	1.1 (0.5)	1.4 (1.6)		2.2
4886-187	270 (360)	0.6 (0.8)	1.0 (0.6)	1.4 (1.6)		2.2
4886-189	370 (450)	3.1 (6.1)	1.1 (1.3)	1.8 (1.8)		1.9

5 The base polymer system composed of butyl acrylate/styrene/acrylic acid (4886-116) displayed tack, shear, and initial peel values in the general range of interest for removable performance. Heat aged peel values, however, show adhesive build to permanent peel levels making an adhesive manufactured from only the emulsion copolymer unsuitable. A lower molecular weight version of the base polymer system (4886-118) was included for comparison and the adhesive made therewith displayed similar characteristics.

10 For copolymer emulsion No. 4886-155, heat aged peel build was substantially reduced and aged free film characteristics remained near initial values. Acrylic acid and acrylamide ratios were varied in the remaining copolymer emulsions in order to optimize performance. Adhesive No. 4886-189 made with copolymer emulsion 4886-189 containing 1% acrylamide and 2.5% acrylic acid displayed an excellent peel profile from initial to heat aged values.

15 The remaining polymer systems were generated to vary bulk polymer composition, cross-link density, and internal steric hindrance. For example, when α -methyl styrene was substituted for styrene (4886-181), an improvement in heat aged peel value was obtained. However, initial tack was depressed below acceptable levels. Divinyl benzene was used in polymer 4886-185 to increase cross-link density; however, a loss of initial tack value also was evidenced. Styrene levels were evaluated at 0-4.5 wt-parts per 100 parts copolymer with the 4.5 wt-part level showing optimum performance characteristics in this series of tests.

EXAMPLE 3

25 A second screen performance evaluation with extended heat aging (70° C for one week) was conducted on five polymer systems compounded with four different wetting agents. Copolymer emulsions Nos. 4886-155 and 4886-189 were carried over from the prior example based on the results reported there. Two additional copolymer emulsions, 4924-4 containing 6.0% styrene and 4924-6 containing 4.5% methyl methacrylate, were added to this performance evaluation. Finally, copolymer emulsion 4817-193 containing 0.5% N-methylol acrylamide was included in the study. The results recorded are set forth below.

TABLE 5

5	Adhesive No.	Surfactant ^(a)	Polyken Tack (g/cc)	180° Shear (hrs/1000 g/ 0.5 in ²)	180° Peel (pounds/inch)		Heat Aged
					15 min	24 hr	
5	4886-155	L-121	230 (230)	5 (6)	0.5 (0.5)	0.9 (1.3)	2.5
		104-E	390 (340)	11 (5)	1.0 (0.7)	1.6 (1.4)	2.5
		GR-5M	180 (240)	2 (6)	0.5 (0.6)	0.6 (1.1)	2.4
		7001	70 (80)	3 (4)	0.2 (0.2)	0.4 (1.2)	0.8
10	4886-189	L-121	270 (320)	5 (4)	0.6 (0.5)	1.3 (1.4)	2.5
		104-E	290 (350)	15 (7)	0.9 (1.2)	1.3 (1.5)	3.3
		GR-5M	280 (350)	6 (18)	1.1 (0.9)	0.9 (1.5)	2.6
		7001	90 (80)	10 (4)	0.4 (0.3)	0.5 (1.2)	1.2
15	4924-4	L-121	330 (320)	3 (10)	1.0 (0.6)	1.6D (1.0)	2.0
		104-E	280 (340)	10 (2)	0.7 (0.9)	1.7 (1.4)	2.4
		GR-5M	280 (290)	6 (12)	0.6 (0.6)	0.6 (1.6)	2.7
		7001	90 (90)	2 (2)	0.6 (0.1)	0.7 (0.6)	1.5
20	4924-6	L-121	330 (245)	15 (44)	1.2 (0.4)	2.2 (1.2)	2.1
		104-E	210 (150)	2 (11)	0.5 (0.9)	1.0 (1.5)	2.2
		GR-5M	290 (350)	36 (24)	1.1 (0.8)	2.5 (1.6)	3.2
		7001	90 (90)	23 (32)	1.1 (0.2)	2.0 (1.1)	1.6
25	4817-193	L-121	240 (300)	4 (6)	1.5 (1.1)	2.5 (1.5)	3.4
		104-E	290 (270)	3 (2)	1.4 (1.0)	2.2 (1.6)	3.4
		GR-5M	240 (250)	2 (11)	1.3 (1.0)	1.6 (1.8)	3.6
		7001	140 (150)	4 (8)	1.9 (0.7)	2.5 (1.7)	2.5
30	(a) Pluronic L-121, See Example 2. Sulfonyl 104-E (50% actives), tetramethyl decyldiol in ethylene glycol, Air Products Company. Triton GR-5M (60% active), dioctyl sodium sulfosuccinate in H ₂ O/isopropanol (80/20 by wt), Union Carbide Corporation						
35	(b) Heat aged at 70° C for one week, then equilibrated to room temperature for 24 hrs. "D" denotes delamination or transfer from Mylar face stock to the stainless steel.						

Adhesive 4817-193 containing N-methylol acrylamide displayed good initial removable performance, though heat aging results showed excessive peel build with values over 3 lbs/in off stainless steel. Emulsion 4886-155, containing a 2:1 acrylic

acid:acrylamide ratio displayed good initial removable performance. Applied heat aging results showed lower peel build with values under 3 lbs/in off stainless steel. Heat aged free film showed good retention of tack and peel characteristics. The version compounded with Sulfonyl 104-E surfactant offered the best performance profile.

Adhesive No. 4886-189, containing a 2.5:1.0 acrylic acid:acrylamide ratio, displayed similar characteristics with higher shear and peel values compared to the 2:1 acid/amide version. Adhesives 4924-4 and 4924-6 were synthesized with additional styrene and methyl methacrylate, respectively, in an attempt to further improve applied heat aging characteristics. The Pluronic L-121 surfactant compounded versions of these systems displayed the best heat aged peel characteristics in the series. The methyl methacrylate modification compounded with Pluronic L-121 (4924-6) demonstrated clean removability and meets the high performance profile ideally possessed by the adhesives of the present invention.

EXAMPLE 4

Three systems (4886-155, 4886-189, and 4924-6) were promoted from the previous example to testing with vinyl face stock. The experimental adhesives were coated at 1 mil dry thickness onto a release liner and then transferred to 3.5 mil vinyl calandered face stock. Extended heat aging at 70° C for one week again was evaluated. Each of the formulations were compounded with 1 wt-% Pluronic L-121 surfactant.

The following results were recorded.

TABLE 6

Adhesive No.	Polyken Tack (g/cc)	180° Shear (hrs/1000 g/0.5 in ²)	<u>180° Peel (pounds/inch)</u>		Heat Aged
			15 min	24 hr	
4886-155	330 (180)	3.9	1.2 (0.4)	1.7 (0.9)	1.7
4886-189	340 (100)	6.1	1.4 (0.2)	1.8 (0.5)	1.6
4924-6	260 (100)	3.2	1.0 (0.1)	1.5 (0.7)	1.6

Adhesives 4886-155 and 189 displayed clean removability. Adhesive 4886-155 exhibited the highest tack retention values and the best retention of adhesive performance yielding a 50% reduction in peel values for heat aged film stock on 24 hr dwell on stainless steel. No peel build or delamination was observed upon applied heat aging. Overall performance was judged to be the best for these adhesives tested. It should be noted that each of these experimental adhesives conform to FDA, 21 CFR Ch. 1, §175.105 making them suitable for indirect contact

with food.

EXAMPLE 5

Long-term removability of removable pressure sensitive adhesives must be achieved with an adhesive of sufficient tack and initial peel properties to provide a satisfactory adhesive bond. In the prior examples, an aqueous emulsion acrylic pressure sensitive copolymer containing specific carboxyl and amide functionality was investigated and determined to provide a significant improvement in heat age removability. In this and some later examples, phosphate surfactants were investigated as candidate surfactants in order to determine whether performance of the adhesives could be improved in accordance with the hydrogen bonding model postulated therefor. Initial research efforts focused on evaluating different types of phosphate surfactants. These surfactants generally are reported to be mixtures of mono and coester phosphates prepared from phosphorous pentoxide and various aliphatic and aromatic alcohols and ethoxylates. Commercially, they typically are supplied as free acids or partially neutralized sodium or potassium phosphates. The candidate phosphate surfactants evaluated are detailed below.

TABLE 7

Product	Manufacturer	Ester Type(s)	Salt/Acid	Activity (wt-%)	pH
Strodex PK-90	Dexter	Aliphatic Ethoxylate	K+	90	10.5 at 100%
Strodex SEK-50	Dexter	Aliphatic Ethoxylate	K+	50	7.0 at 100%
Gafac RD-510	GAF	Dodecyl Ethoxylate	Acid	98	<1.5 at 10%
Gafac LO-529	GAF	Nonyl Phenol Ethoxylate	Na+	88	5-6 at 10%
Gafac RE-610	GAF	Nonyl Phenol Ethoxylate	Acid	100	<1.5 at 10%
Phosfac 8608	Colloids Lyndal	Nonyl Phenol Ethoxylate	Acid	95-100	<3 at 1%
Phosfac 9606A	Colloids Lyndal	Nonyl Phenol Ethoxylate	Acid	>99	<2.5 at 1%
Phosfac 9608-ME	Colloids Lyndal	Nonyl Phenol Ethoxylate	Acid	100	3.0 at 1%
Phosfac 9609	Colloids Lyndal	Nonyl Phenol Ethoxylate	Acid	100	3.0 at 1%
Triton QS-44	Union Carbide	*	Acid	80	1.6 at 1%
Triton H-66	Union Carbide	*	K+	50	8-10 at 5%
Emphos D70-30C	Witco	Glyceryl Oleate	Na+	83-87	6.5 at 3%
Emphos CS-141	Witco	--	--	--	--

*No information available from product literature.

Initial evaluation included simple addition of the phosphate surfactant candidate to the adhesive formulation and basification with ammonia. The aqueous acrylic emulsion copolymer was synthesized with the ingredients and ratios set forth for emulsion copolymer number 4886-155. The following results were

5 recorded:

TABLE 8

	Adhesive		Ammonia ^b	pH	Polyken Tack (g)	180° Peel Adhesion ^(c) (lbs/in)			
	No. 4924	Surfactant ^a				30 min	24 hr	Heat Aged	Time
5	145	Strodex PK-90	No	4.3	340	0.5	--	1.3	40 hrs
	145	Strodex PK-90	Yes	5.6	310	0.8	--	0.7	40 hrs
	145	Gafac RD-510	No	2.1	280	0.2	--	0.6	40 hrs
	145	Gafac RD-510	Yes	6.2	300	0.2	--	0.5	40 hrs
	145	Gafac LO-529	No	2.9	360	0.9	--	2.2	40 hrs
10	145	Gafac LO-529	Yes	5.3	250	0.4	--	1.5	40 hrs
	145	Gafac RE-610	No	2.1	370	0.9	--	2.7	40 hrs
	145	Gafac RE-610	Yes	5.1	330	0.9	--	2.4	40 hrs
	145	Phosfac 8608	No	2.1	370	1.2	--	2.4	40 hrs
	145	Phosfac 8608	Yes	5.1	320	0.9	--	2.4	40 hrs
15	145	Phosfac 9606A	No	2.2	330	1.0	--	2.5	40 hrs
	145	Phosfac 9606A	Yes	4.8	370	0.7	--	1.9	40 hrs
	145	Phosfac 9608-ME	No	2.2	360	1.0	--	2.5	40 hrs
	145	Phosfac 9608-ME	Yes	4.8	320	0.7	--	1.9	40 hrs
	145	Phosfac 9609	No	2.2	350	0.8	--	2.4	40 hrs
20	145	Phosfac 9609	Yes	5.4	310	0.7	--	1.9	40 hrs
	178	Strodex SEK-50	No	3.2	350	0.3	0.8	1.9	3 days
	178	Strodex SEK-50	Yes	6.8	260	0.5	0.5	1.6	3 days
	178	Triton H-66	No	5.2	240	0.5	1.1	1.6	3 days
	178	Triton H-66	Yes	6.2	310	1.1	1.5	2.1	3 days
25	178	Triton QS-44	No	2.0	330	1.0	0.9	2.0	3 days
	178	Triton QS-44	Yes	7.0	370	0.9	1.1	2.4	3 days
	178	Emphos D70-30C	No	2.8	-----uncoatable-----				
	178	Emphos D70-30C	Yes	5.6	-----uncoatable-----				
	178	Emphos CS-141	No	2.8	360	0.6	1.1	2.7	3 days
30	178	Emphos CS-141	Yes	5.6	360	0.7	0.6	1.7	3 days

(a) Added 1.0 wt-% active to base latex polymer.

(b) Diluted ammonia (14%) addition for basification and thickening.

(c) 1 mil coating on H.P. Smith 8024 transfer coated to 2 mil Mylar.

35 The above-tabulated results demonstrate that different types of phosphate surfactants cause considerable augmentation in peel strength, suggesting a significant phosphate-polymer substrate interaction. The effect of basification also can be seen by reviewing these results.

EXAMPLE 6

Five of the phosphate surfactants evaluated in Example 5 were selected for further evaluation: Strodex PK-90, Strodex SEK-50, Triton H66, Gafac RD-510, and Emphos CS-141. Each of these surfactants exhibited low adhesion build characteristics in the initial performance screen evaluation. In this example, these surfactants were compounded with four different basification reagents and submitted to testing as described above. The following results were recorded.

TABLE 9

Surfactant (1 wt-% actives)		Base(a)	pH	Viscosity (cps)	180° Peel (lbs/in) 30 min Heat Aged(c)	
	None	None	2.7	40	—(d)	—
5	Strodex PK-90	None	4.2	90	—	—
	Strodex PK-90	NH ₃	8.6	1770	0.7	1.8
	Strodex PK-90	AMP-95	8.7	2100	0.8	1.8
	Strodex PK-90	CORCAT P-12	10.0	700	0.9	3.7
10	Strodex PK-90	KOH	8.9	1800	0.3	1.0
	Strodex SEK-50	None	3.1	40	—	—
	Strodex SEK-50	NH ₃	9.0	1950	0.5	1.5
	Strodex SEK-50	AMP-95	9.1	3100	0.6	1.5
15	Strodex SEK-50	CORCAT P-12	9.8	800	1.3	4.5
	Strodex SEK-50	KOH	9.4	3000	0.9	1.6
	Triton H-66	None	5.0	190	—	—
	Triton H-66	NH ₃	9.0	1100	0.9	1.6
20	Triton H-66	AMP-95	9.1	2150	0.9	2.4
	Triton H-66	CORCAT P-12	9.7	1100	0.8	2.3
	Triton H-66	KOH	8.8	1100	0.7	1.8
	Gafac RD-510	None	2.1	30	—	—
25	Gafac RD-510	NH ₃	8.7	800	0.2	0.4
	Gafac RD-510	AMP-95	8.3	820	0.0	1.0
	Gafac RD-510	CORCAT P-12	-----unstable-----			
	Gafac RD-510	KOH	8.2	450	0.0	—
30	Emphos CS-141	None	2.2	40	—	—
	Emphos CS-141	NH ₃	8.9	1600	0.8	3.0
	Emphos CS-141	AMP-95	9.1	2300	1.2	2.2
	Emphos CS-141	CORCAT P-12	9.8	500	0.7	3.2
	Emphos CS-141	KOH	8.0	400	0.5	1.4
35	(a)	NH ₃ at 14 wt-% concentration. AMP-95 is 2-amino-2-methylpropanol, Angus Chemical Company. CORCAT P-12 is polyethyleneimine, Virginia Chemical Company. All heat aged films yellowed. KOH at 20 wt-% concentration.				
40	(b)	Brookfield RVT at 25° C.				
	(c)	90 hours at 70° C.				

(d) Dashed entries indicate that the latex was not coatable on release paper.

These results demonstrate that emulsion copolymer viscosity, peel adhesion, and heat age performance are affected both by phosphate ester type and by the type of base reagent. Strodex PK-90 and SEK-50 basified with ammonia or potassium hydroxide yielded the best removable performance. Gafac RD-510 basified with ammonia afforded an ultra-removable performance profile. It is interesting to note the strong viscosity suppression that Gafac RD-510 also exhibited. This indicates a strong affinity between phosphate surfactant and carboxylate swelled layers of the copolymer particles.

EXAMPLE 7

The Strodex surfactants evaluated in Example 6 were further evaluated with ammonia (14 wt-% concentration) and potassium hydroxide (20 wt-% concentration) basification. In this series of runs, adhesive films were dried for different periods in a forced air oven to determine the effect of residual volatile components on adhesive performance. The heat aged data was determined after subjecting the samples to a temperature of 70° C for 72 hours. The following data was recorded.

20

TABLE 10

Surfactant (1 wt-% actives)	Base	pH	(min)	178° Shear (hrs/100 g 0.5 in ²)	90° Peel (lb/in)		180° Peel (lb/in)	
					20 min	Heat Aged	30 min	Heat Aged
Strodex PK-90	NH ₃	8.4	2	22	0.7	1.7	0.6	2.0
Strodex PK-90	NH ₃	8.4	20	14	0.6	1.1	0.3	1.5
Strodex PK-90	KOH	8.5	2	71	0.5	0.8	0.2	1.8
Strodex PK-90	KOH	8.5	20	44	0.6	0.5	0.1	0.7
Strodex SEK-50	NH ₃	8.6	2	17	0.4	1.2	0.5	2.6
Strodex SEK-50	NH ₃	8.6	20	7	0.6	1.2	0.3	1.9
Strodex SEK-50	KOH	8.7	2	78	0.3	1.1	0.2	1.7
Strodex SEK-50	KOH	8.7	20	63	0.7	1.1	0.2	1.7

These results indicate that 20 minutes drying time generally yielded low peel values. The comparison between ammonia and potassium hydroxide showed the non-volatile basification as affording lower peel and higher shear values, demonstrating a pronounced effect on film formation and interfacial adhesion.

In total, the results reported in Examples 5-7 demonstrate that aliphatic ethoxylated phosphate esters yielded the best performance properties and strongest interactions. These results further demonstrate that compounding ingredients, such as phosphate ester surfactants, is a technique that can be used to manipulate aqueous emulsion acrylic pressure sensitive adhesive performance. The acrylic latex systems reported herein are receptive to basification and interfacial phenomena additionally. All adhesives are self-thickening upon basification both with aqueous ammonia and potassium hydroxide solutions. Strodx PK90 or SEK-50 appear to be the preferred phosphate ester surfactants evaluated in the development of high performance removable acrylic emulsion pressure sensitive adhesive products. Gafac RD-510 appeared to be suitable for developing an ultra-removable product.

EXAMPLE 8

Emulsion polymerizations of n-butyl acrylate/styrene copolymers ranging from 0.0 to 20.0 monomer wt-% acrylamide and/or acrylic acid are summarized in Table 11 below. Polymerizations conducted with 0.0 to 3.0 wt-% acrylamide and 0.0 to 2.0 wt-% acrylic acid were reacted to a nominal 60 wt-% polymer content. Those polymerizations conducted with higher levels of acrylamide and acrylic acid were reacted with abbreviated delayed feeds to a nominal 40 wt-% polymer content to prevent extreme viscosity increases in the later stages of emulsion polymerization. The standard acrylamide/acrylic acid composition of 1.0/2.0 wt-% (4886-155 of Table 1) was prepared at both 60% nv solids (5042-154) and 40% nv solids (5042-158) to determine the effect of lower polymerization solids content on the physical and adhesive characteristics of these emulsion polymer systems and to provide a lower acrylamide/acrylic acid composition reference at 40 wt-% reacted polymer solids.

TABLE 11

Emulsion Polymerization ^a Summary
Acrylamide (AMD) Acrylic Acid (AA) Variations

5	Polymer		Final ^c		Particle ^d size (nm)
	Laboratory	Composition ^e AMD/AA/STY/BA	Final Solids ^b	Viscosity (cps)	
10	5042-89	1.0/0.0/4.5/94.5	58.9	1650	250
	5042-170	1.0/1.0/4.5/93.5	60.4	2130	220
	5042-154	1.0/2.0/4.5/92.5	58.9	1600	240
	5042-156	1.0/3.0/4.5/91.5	58.1	3270	330
	5042-160	1.0/5.0/4.5/89.5	38.6	12	200
	5042-162	1.0/10.0/4.5/84.5	38.5	20	240
	5042-178	1.0/20.0/4.5/74.5	39.5	2180	400
	5042-29	0.0/2.0/4.5/93.5	59.8	690	250
15	5042-154	1.0/2.0/4.5/92.5	58.9	1600	240
	5042-31	2.0/2.0/4.5/91.5	55.2	160	370
	5042-168	5.0/2.0/4.5/88.5	38.2	12	220
	5042-164	10.0/2.0/4.5/83.5	39.0	1360	400
	5042-180	20.0/2.0/4.5/73.5	39.9	960	240
20	5042-166	5.0/5.0/4.5/85.5	38.7	25	270
	5042-158	1.0/2.0/4.5/92.5	38.8	12	170

a) All emulsion polymerizations were conducted in deionized water with pre-emulsified monomer in deionized water containing 9.0% (phm) Triton X-200 surfactant. Polymerizations were initiated with 21.4 grams of monomer emulsion in 230 grams deionized water with a sodium bisulfite/potassium persulfate initiator system. Reactions were carried out at 80°C with delayed monomer emulsion and potassium persulfate solution additions over a three hour period. See 4886-155 or 5042-154 as standard examples.

b) Non-volatile weight percent.
c) Brookfield RVF viscosity at 20 rpm, 25°C.
d) Unimodal distribution means obtained on a Coulter Model N4 particle size analyzer.

e) AMD = Acrylamide
AA = Acrylic Acid
STY = Styrene
BA = n-Butyl Acrylate.
Polymer composition in monomer weight percent.

40 All emulsion polymers reported above were found to be stable. The comparison of the preferred composition (4886-155) reacted to 60 wt-% solids (5042-154) and 40 wt-% solids (5042-158) reveals that a significant reduction in mean particle diameter is obtained when delayed feeds are terminated early to afford 40 wt-% solids, viz, 240 nm vs 170 nm, respectively.

Compounding of the base latex polymers was conducted with Strodex SEK-50 phosphate surfactant (2.0 wt-% dry/dry polymer) and basified with aqueous ammonia. These compositions are summarized in Table 12.

TABLE 12
Compounding Summary
Acrylamide Acrylic Acid Variations

Laboratory Reference	Base Latex Polymer Reference	Latex (grams)	Latex Solids Wt-%	D.I. Water (grams)	Strodex ^a SEK-50 (grams)	Colloid 679 (grams)	Aqua ^b Ammonia (14%) (grams)
5042-184A	5042-154	150	58.9	20	3.5	0.3	1.5
5042-184B	5042-158	150	38.8	0	2.3	0.3	2.5
5042-184C	5042-29	150	59.8	0	3.6	0.3	1.5
5042-184D	5042-89	150	58.9	0	3.5	0.3	1.5
5042-184E	5042-170	150	60.4	20	3.6	0.3	1.8
5042-184F	5042-156	150	58.1	20	3.5	0.3	1.6
5042-184G	5042-160	150	38.6	0	2.3	0.3	2.0
5042-184H	5042-162	150	38.5	0	2.3	0.3	2.2
5042-184I	5042-31	150	55.2	15	3.3	0.3	2.0
5042-184J	5042-168	150	38.2	0	2.3	0.3	2.2
5042-184K	5042-166	150	38.7	0	2.3	0.3	2.1
5042-184L	5042-164	150	39.0	0	2.3	0.3	1.2
5042-184M	5042-178	150	39.5	0	2.4	0.3	1.5
5042-184N	5042-180	150	39.9	0	2.4	0.3	2.5

a) 2.0 wt-% dry phosphate surfactant on dry emulsion polymer level

b) All emulsions were basified with 14% aqua ammonia. Adhesives were transfer coated if an increase in viscosity was obtained. Adhesives that did not thicken with basification were direct coated.

All adhesive compositions reported above afforded uniform films when cast on release liner or polyester film. The adhesive properties of these compositions is set forth in Table 13.

5

TABLE 13
Adhesive Performance Summary^a
Initial Film and (Aged Film)^j Properties
Acrylamide Acrylic Acid Variations

Laboratory Reference	Polymer ^b Composition AMD/AA/STY/BA	180° Peel (oz/in)			Loop Tack (lbs/in)	Polyken Tack (grams)	Shear 1" x 1/2" x 1 kg (hrs)	Coating Method	
		Dwell Time		Week 70°C					
		30 min.	24 Hr.						
5041-184D	1.0/0.0/4.5/94.5	2.6 (1.5)	1.0 (1.4)	3.1	25.0	1.0 (1.3)	250 (310)	2.3 C (2.3 C)	Transfer
5042-184E	1.0/1.0/4.5/93.5	4.1 (2.2)	3.5 (3.1)	9.4	18.0	1.0 (0.9)	210 (260)	7.8 C (10.0 C)	Transfer
5042-184A	1.0/2.0/4.5/92.5	5.6 (3.1)	7.4 (12.2)	11.4	27.3	0.9 (0.6)	200 (300)	10.4 C (21.1 C)	Transfer
5042-184F	1.0/3.0/4.5/91.5	2.6 (2.1)	8.2 (11.1)	20.6	22.6	0.9 (0.7)	180 (310)	12.4 PD (18.9 PD)	Transfer
5042-184G	1.0/5.0/4.5/89.5	3.5 (1.6)	1.3 (20.8)	28.1	38.2	0.9 (0.7)	180 (220)	37.5 D (33.2 D)	Transfer
5042-184H	1.0/10.0/4.5/84.5	2.8 (3.2)	19.2 (17.8)	33.1	25.4	0.8 (0.8)	80 (170)	140 D (24 D)	Transfer
5042-184M	1.0/20.0/4.5/74.5	2.2 (0.4)	19.2 D (4.7)	11.5 D	34.3 C	0.4 (0.0)	0 (0)	> 240	Transfer
5042-184C	0.0/2.0/4.5/93.5	13.4 (13.4)	12.2 (17.6)	18.9	33.4	1.2 (0.9)	220 (370)	3.1 C (2.5 C)	Transfer
5042-184I	2.0/2.0/4.5/91.5	2.6 (1.2)	1.0 (2.0)	17.5	24.2	1.0 (0.7)	250 (190)	2.3 PD (3.9 A)	Transfer
5042-184J	5.0/2.0/4.5/88.5	0.9 (0.6)	1.6 (1.1)	27.7	37.0	0.5 (0.6)	110 (200)	23.6 PD (4.8 A)	Direct
5042-184L	10.0/2.0/4.5/83.5	0.6 (0.3)	1.4 (0.5)	5.8	20.9	0.2 (0.0)	0 (40)	1.0 A (5.3 PD)	Transfer
5042-184N	20.0/2.0/4.5/73.5	0.0 (0.0)	0.0 (0.0)	0.9	0.0	0.0 (0.0)	0 (0)	0 (0)	Direct
5042-184K	5.0/5.0/4.5/85.5	0.7 (0.9)	12.8 (1.8)	44.1	34.8	0.5 (0.6)	80 (200)	13 A (12 A)	Transfer
5042-184A	1.0/2.0/4.5/92.5	5.9 (4.9)	9.6 (8.0)	20.1	25.4	1.1 (0.6)	300 (300)	14.9 C (21.3 C)	Direct
5042-184B	1.0/2.0/4.5/92.5	6.3 (2.4)	10.8 (19.0)	21.3	41.0	1.0 (0.6)	240 (380)	15.7 C (8.9 C)	Direct

Footnotes to Table 13

- 5 a) Adhesive evaluations were conducted with 1.0 ± 0.1 mil dry adhesive films transfer coated from H.P. Smith 8024 release liner to 2 mil polyester film or direct coated to 2 mil polyester film. All testing was conducted off stainless steel. Results are recorded in laboratory notebooks C5041 and C5121. All adhesive failures are adhesive unless otherwise noted as follows:
A = Adhesive
C = Cohesive
D = Delamination
- 10 b) AMD = Acrylamide
AA = Acrylic Acid
STY = Styrene
BA = n-Butyl Acrylate.
Polymer composition in monomer weight percent

15

The above-tabulated results indicate a copolymer content of about 1.0 wt-% acrylamide and 1.0 to 2.0 wt-% acrylic acid (5042-184A and 5042-184E) afford an optimum removable pressure sensitive adhesive performance profile as judged by initial and heat aged peel values. Higher acrylic acid levels generally afford higher peel values after room temperature dwell periods of 24 hours and one week. Higher acrylamide levels generally afford lower initial and applied heat aged peel values. Thus, a combination of these two functional monomer effects appears to yield an optimum adhesive performance profile with good initial peel and tack values, and a minimum peel build upon applied heat aging.

25 Comparison also was made between the AMD/AA/STY/BA (1.0/2.0/4.5/92.5) polymer reacted to 60 and 40 wt-% emulsion polymer solids (5042-184A and 5042-184B, respectively). The direct coated comparison shows higher applied heat aged peel values are obtained for the 40 wt-% solids emulsion polymerization. This may be related to the smaller mean particle size obtained for this polymerization emulsion copolymer morphology and film formation effects.

30

EXAMPLE 9

35 Carboxylic acid-bearing ethylenically-unsaturated monomers were evaluated at equivalent acid stoichiometries in order to determine the effect of carboxylic acid structure on polymer adhesive performance. Copolymerizations of the preferred 4886-155 copolymer were conducted with methacrylic acid, crotonic acid, itaconic acid, fumaric acid, and β -carboxyethyl acrylate. These emulsion polymerizations are summarized in Table 14 below.

TABLE 14
Emulsion Polymerization ^a Summary
Carboxylic Monomer Variations

Laboratory Reference	Acid Bearing Monomer	MW (g mole ⁻¹)	Carboxylic ^b Equivalent Weight (phm)		Polymer Composition ^c AMD/Acid/STY/BA	Final ^d Solids (wt-%)	Final ^c Viscosity (cps)	Final pH	Particle Size (nm)
5042-154	Acrylic Acid	72.06	2.00		1.00/2.00/4.50/92.50	58.9	1600	2.3	240
5042-172	Methacrylic Acid	86.09	2.19		1.00/2.19/4.50/92.31	59.1	1310	2.4	230
5042-174	Crotonic Acid	86.09	2.19		1.00/2.19/4.50/92.31	58.0	1150	2.3	230
5042-176	β -CEA	144.12	4.00		1.00/4.00/4.50/90.50	57.1	1100	3.5	260
5042-182	Itaconic Acid	130.10	1.80		1.00/1.80/4.50/92.70	58.9	390	2.7	270
5042-185	Fumaric Acid	116.07	1.61		1.00/1.61/4.50/92.89	58.9	390	2.4	280

Footnotes to Table 14

- 5 a) All emulsion polymerizations were conducted in deionized water with pre-emulsified monomer in deionized water containing 9.0% (phm) Triton X-200 surfactant. Polymerizations were initiated with 21.4 grams of monomer emulsion in 230 grams deionized water with a sodium bisulfite potassium persulfate initiator system. Reactions were carried out at 80°C with delayed monomer emulsion and potassium persulfate solution additions over a three hour period. See 4886-155 or 5042-154 as standard examples.
- 10 b) Copolymer weight percents yielding equal carboxylic functionality or equivalent copolymer acid value.
- 15 c) AMD = Acrylamide
AA = Acrylic Acid
STY = Styrene
BA = n-Butyl Acrylate.
Polymer composition in monomer weight percent.
- d) Non-volatile weight percent
- 20 e) Unimodal distribution means obtained on a Coulter Model N4 particle size analyzer.

Compounding of the adhesive compositions was conducted with 2.0 wt-% (dry/dry polymer) Strodex SEK-50 phosphate surfactant, Colloid 679 defoamer, and aqueous ammonia to afford pressure sensitive adhesives. The compositions are set forth in Table 15 below.

TABLE 15

Compounding Summary

Carboxylic Monomer Variations

30	Laboratory Reference	Base Latex Polymer Reference	Latex (grams)	Latex Solids Wt-%	D.I. Water (grams)	Strodex ^a SEK-50 (grams)	Colloid 679 (grams)	Aqua ^b Ammonia (14%)(grams)
	5042-184A	5042-154	150	58.9	20	3.5	0.3	1.5
	5042-195A	5042-172	150	59.1	0	3.6	0.3	1.5
35	5042-195B	5042-174	150	58.0	0	3.5	0.3	4.0
	5042-195C	5042-176	150	57.1	0	3.4	0.3	0.5
	5042-195D	5042-182	150	58.9	0	3.5	0.3	4.0
	5042-195E	5042-185	150	58.9	0	3.5	0.3	4.0

- 40 a) 2.0 wt-% dry phosphate surfactant on dry emulsion polymer level.
- b) All emulsions were basified with 14% aqua ammonia. Adhesives were transfer coated if an increase in viscosity was obtained. Adhesives that did not thicken with basification were direct coated.

Adhesive performance results recorded are set forth in Table 16.

TABLE 16
Adhesive Performance Summary^a
Initial Film and (Aged Film)^b Properties
Carboxylic Monomer Variations

Laboratory Reference	Acid Bearing Monomer	180° Peel (oz/in)			Loop Tack (lbs/in)	Polyken Tack (grams)	Shear 1" x 1/2" x 1 kg (hrs)	Coating Method
		Dwell Time 30 min.	24 Hr.	Week				
5042-184A	Acrylic Acid	6.2 (10.9)	8.7 (11.2)	11.6	25.8	200 (320)	10.8 A (19.6 C)	Transfer
5042-195A	Methacrylic Acid	3.5 (2.7)	5.4 (4.0)	6.5	22.0	190 (240)	5.9 C (9.4 C)	Transfer
5042-195B	Crotonic Acid	4.0 (2.5)	7.9 (5.2)	9.3	27.6	220 (300)	2.5 C (3.4 C)	Transfer
5042-195C	β-CEA	2.7 (3.5)	3.6 (5.8)	16.0	17.8	220 (230)	4.5 D (12.2 C)	Transfer
5042-195D	Itaconic Acid	10.6 (5.0)	14.8 (12.9)	12.2	26.9	260 (330)	5.9 C (>233)	Transfer
5042-195E	Fumaric Acid	10.4 (4.0)	15.0 (6.8)	14.2	30.2	180 (210)	10.3 C (>233)	Direct

a) Adhesive evaluations were conducted with 1.0 ± 0.1 mil dry adhesive films transfer coated from H.P. Smith 8024 release liner to 2 mil polyester film or direct coated to 2 mil polyester film. All testing was conducted off stainless steel. Results are recorded in laboratory notebooks C5041 and C5121.

b) All adhesive failures are adhesive unless otherwise noted as follows: A = Adhesive, C = Cohesive, D = Delamination. Peel tests were conducted under PSTC-1 conditions. Heat aging was conducted at 70°C (158°F) in forced air ovens for one week. Data for films heat aged on liner prior to adhesive testing is in parentheses. All heat aged films and laminates were re-equilibrated to 72°F 50% relative humidity for one day prior to testing.

These results demonstrate lower peel values for less hydrophilic carboxylic acid copolymers (*i.e.* methacrylic acid, crotonic acid, and β -CEA) and higher peel values for more hydrophilic carboxylic acid copolymers (*i.e.* itaconic acid and fumaric acid) compared to the acrylic acid copolymer 5042-184A. The itaconic acid and fumaric acid copolymers also afforded adhesive films that exhibited high cohesive strength after heat aging on liner. β -carboxyethyl acrylate exhibited the lowest peel value after applied heat aging.

EXAMPLE 10

Preferred emulsion copolymer 4886-155 is prepared by semi-batch emulsion polymerization with a uniform monomer feed containing n-butyl acrylate/styrene/ acrylic acid/ acrylamide (92.5/4.5/2.0/1.0). The data presented above demonstrates that the acrylic acid and acrylamide polymer content are important structural parameters affecting adhesive performance when the carboxylic acid and amide functionalities are copolymerized. This example extends the use of carboxylic and amide functional polymers in removable emulsion pressure sensitive adhesives to include polymer architectures other than simple copolymerizations of uniform monomer mixtures.

Several different macromolecular arrangements of carboxylic and amide functional polymers were investigated as follows:

1. Simple emulsion copolymerization of carboxyl and amide-bearing monomers with acrylate ester (4886-155).
2. Emulsion polymer physical blend of a carboxylated acrylic latex and an amide functional acrylic latex.
3. A combination of a functional aqueous colloidal polymer and functional water soluble polymer.
 - (a) Carboxylated acrylic emulsion copolymer modified with polyacrylamide solution polymer.
 - (b) Acrylamide-containing acrylic emulsion copolymer modified with polyacrylic acid solution polymer.
4. Interpenetrating emulsion polymer networks containing carboxylic and amide functionalities.
 - (a) Polymerization of an interpenetrating acrylamide copolymer with an acrylic acid copolymer.
 - (b) Polymerization of an interpenetrating acrylic acid copolymer with an acrylamide copolymer.

These structural polymer variations were prepared to yield equivalent aggregate compositions. The synthesis thereof is summarized in Table 17 below.

TABLE 17

Emulsion Polymerization a Summary

Laboratory Reference	Polymer ^b Type	Polymer ^b Composition AMD/AA/STY/BA	Final ^c Solids (wt-%)	Final ^d Viscosity (cps)	Final pH	Particle ^e Size (nm)
5042-154	1 x AA	1.0/2.0/4.5/93.5	58.9	1600	2.3	240
	1 x AMD					
	Single Stage					
5042-29	1 x AA	0.0/2.0/4.5/93.5	59.8	690	2.2	250
	Single Stage					
5042-89	1 x AMD	1.0/0.0/4.5/94.5	58.9	1650	2.3	250
	Single Stage					
5121-8	2 x AA	0.0/4.0/4.5/91.5	57.9	700	2.6	240
	Single Stage					
5121-10	2 x AMD	2.0/0.0/4.5/93.5	55.9	2850	2.7	270
	Single Stage					
4864-82	Two Stage IPN ^f	1) 0.0/4.0/4.5/91.5 2) 2.0/0.0/4.5/93.5	58.0	490	2.1	290 ^g
4864-84	Two Stage IPN ^f	1) 2.0/0.0/4.5/93.5 2) 0.0/4.0/4.5/91.5	54.7	670	2.0	310 ^g

Footnotes to Table 17

- 5 a) All single stage emulsion polymerizations were conducted in deionized water with pre-emulsified monomer in deionized water containing 9% (phm) Triton X-200 surfactant. Polymerizations were initiated with 21.4 grams of monomer emulsion in 230 grams deionized water with a sodium bisulfite potassium persulfate initiator system. Reactions were carried out at 80°C with delayed monomer emulsion and potassium persulfate solution additions over a three hour period.
- 10 b) AMD = Acrylamide, AA = Acrylic Acid, STY - Styrene, BA = n-Butyl Acrylate
Polymer composition in monomer weight percent
- c) Non-volatile weight percent
- d) Brookfield RVF viscosity at 20 rpm, 25°C
- 15 e) Unimodal distribution means obtained on a Coulter Model N4 particle size analyzer.
- f) Interpenetrating emulsion polymers were prepared using equal weights of seed emulsion (5121-8 & 5121-10) dry polymer and interpenetrating second stage monomers. Initial IPN reaction conditions were adjusted to represent the continuous feed reaction (4886-155, 5042-154, APS-1184) at 50% delayed monomer feed reacted.
- 20 The monomer emulsion was added to the first stage emulsion polymer, mixed for 30 minutes, and reacted in two portions.
The resulting overall monomer and surfactant compositions for the acrylamide IPN (4864-82), acrylic acid IPN (4864-84), and continuous polymerization (4886-155, 5042-154) are identical. Experimental details can be found in laboratory notebook 4864.
- 25 g) The 40 and 50 nm increase in mean particle size for interpenetrating polymers 4864-82 and 4864-84 over the seed latexes 5121-8 and 5121-10 is evidence of interpenetrating polymer formation. Particle volume increases are about 70% of theoretical.
- 30

The emulsions were all compounded with phosphate coester surfactant and basified with aqueous ammonia to afford pressure sensitive adhesives. This

35 compounding is summarized in Table 18 below.

TABLE 18
Compounding Summary

Laboratory Reference	Carboxyl Polymer Source (g)	Amide Polymer Source (g)	Deionized Water (g)	Strodxg SEK-50 (g)	Colloids 679 (g)	Aqua ^h Ammonia (g)
5042-184A	Acrylic Acid Containing Acrylic Emulsion Polymer 5042-29 150.0	Acrylic Acid-Acrylamide Containing Acrylic Emulsion Copolymer 5042-154 (4886-155) 150.0	20.0	3.5	0.3	1.5
5042-184C		None	0.0	3.6	0.3	1.5
5121-17	Acrylic Acid Containing Acrylic Emulsion Polymer 5042-29 150.0	Polyacrylamide 5% Aqueous Solution 18.0	0.0	3.6	0.3	1.5
5042-184D	None	Acrylamide Containing Acrylic Emulsion Polymer 5042-89 150.0	0.0	3.6	0.3	1.5
5121-16	Polyacrylic Acid 5% Ammoniated Aqueous Solution 36.0	Acrylamide Containing Acrylic Emulsion Polymer 5042-89 150.0	0.0	3.5	0.3	1.5
5121-18A	Acrylic Acid (2X) Containing Acrylic Emulsion Polymer 5121-8 150.0	None	10.0	3.6	0.3	1.0

TABLE 18 (cont'd)
Compounding Summary

Laboratory Reference	Carboxyl Polymer Source (g)	Amide Polymer Source (g)	Deionized Water (g)	Strodex ^a SEK-50 (g)	Colloids 679 (g)	Aqua ^b Ammonia (g)
5121-18B	None	Acrylamide (2X) Containing Acrylic Emulsion Polymer 5121-10 150.0	0.0	3.6	0.3	1.0
5121-18C	Acrylic Acid (2X) Containing Acrylic Emulsion Polymer 5121-8 75.0	Acrylamide (2X) Containing Acrylic Emulsion Polymer 5121-10 75.0	0.0	3.6	0.3	1.0
5121-48A	Seed Polymer Acrylic Acid Containing Emulsion Polymer 5121-8	Interpenetrating Acrylamide Containing Acrylic Emulsion Polymer 4864-82 100.0	12.0	2.0	0.2	2.0
5121-48B	Interpenetrating Acrylic Acid Containing Acrylic Emulsion Polymer 4864-84 100.0	Seed Polymer Acrylamide Containing Acrylate Emulsion Polymer 5121-10	6.0	2.0	0.2	2.0

a) 2.0 wt-% dry phosphate surfactant on dry emulsion polymer level.

b) All emulsions were basified with 14% aqua ammonia until an increase in viscosity was obtained.

Adhesive performance results recorded are set forth in Table 19.

TABLE 19

Adhesion Performance Summary^a
Initial Film and (Aged Film) Properties^b

Laboratory Reference	Polymer Architecture	Dwell Time			Loop Tack		Polyken Tack (g)	Shear 1" x 1/2" x 1 kg (hrs)
		30 min.	24 Hr.	Week	70°C	(lbs/in)		
5042-184A	AA/AMD Emulsion Copolymer	5.6 (3.1)	7.4 (12.2)	11.4	27.3	0.9 (0.6)	200 (300)	10.4 C (21.1 C)
5121-18A	AA X2 Emulsion Polymer	8.3 (8.0)	9.6 (15.4)	26.5	35.0	1.2 (0.5)	150 (260)	34.5 D (14.0 C)
5121-18B	AMD X2 Emulsion Polymer	1.6 (1.4)	2.0 (2.1)	12.4	20.0	0.8 (0.6)	210 (240)	1.1 A (0.8 A)
5121-18C	AA X2 Emulsion AMD X2 Emulsion 1:1 Polymer Blend	4.5 (5.5)	7.4 (8.2)	14.0	21.0	0.8 (1.0)	170 (310)	15.4 (22.1 C)
5042-184C	AA Emulsion Polymer	13.4 (13.4)	12.2 (17.6)	18.9	33.4	1.2 (0.9)	220 (370)	3.1 C (2.5 C)
5121-17	AA Emulsion Polymer AMD Aqueous Polymer Blend	13.0 (0.7)	11.6 (1.2)	21.4	29.6	0.7 (1.1)	155 (310)	3.8 C (1.3)
5042-184D	AMD Emulsion Polymer	2.6 (1.5)	1.0 (1.4)	3.1	25.0	1.0 (1.3)	250 (310)	2.3 C (2.3 C)
5121-16	AMD Emulsion Polymer AA Aqueous Polymer Blend	6.2 (2.9)	4.6 (3.7)	16.0	22.2	0.9 (0.7)	90 (270)	0.8 C (1.6 C)
5121-48A	AMD IPN Emulsion Polymer	9.4 (3.0)	15.1 (6.4)	16.1	24.8	1.0 (0.7)	310 (250)	10.7 D (24.6 PD)
5121-48B	AA IPN Emulsion Polymer	14.2 (3.8)	18.5 (10.9)	19.2	21.8	1.1 (1.1)	270 (210)	8.6 D (11.4 PD)

Footnotes to Table 19

- a) Adhesive evaluations were conducted with 1.0 ± 0.1 mil dry adhesive films transfer coated from H.P. Smith 8024 release liner to 2 mil polyester film. All testing was conducted off stainless steel.
- 5 b) Peel tests were conducted under PSTC-1 conditions. Heat aging was conducted at 70°C (158°F) in forced air ovens for one week. Data for films heat aged on liner prior to adhesive testing is in parenthesis. All heat aged films and laminates were re-equilibrated to 70°F 50% relative humidity for one day prior to testing.

10

Polymer architecture 1 is the basis for the work reported in the previous examples. Adhesives prepared from this polymer system with copolymerization of 1 wt-% acrylamide and 2 wt-% acrylic acid typically exhibit 0.5 to 1.0 lbs/in of initial peel, building to about 1.5 lbs/in of peel after aging at 70° C. Loop tacks are about 1.0 lbs/in. This is the performance reference for the other polymers.

15

Emulsion Blends of Carboxyl and Amide-Containing Latices

The foregoing data in Table 19 summarizes the adhesive performance characteristics for 5121-18C, an adhesive prepared with an equal weight blend of carboxylated acrylate and amide-containing acrylate emulsions. Performance properties were found to be very similar to the acrylic acid-acrylamide copolymer system 5042-184A and intermediate between the adhesive properties of the separate component emulsions, viz, 5121-18A and 5121-18B.

20

The emulsion polymer blend adhesive exhibited the higher initial peel values of the carboxylated latex and the lower heat-aged peel build of the acrylamide latex. These results indicate higher performing water-borne acrylic emulsion pressure sensitive adhesives can be prepared with latex blends. Also, latex blend ratios may provide specific control over removable adhesive performance. This latter feature would permit greater formulation latitude in developing specialty adhesives.

25

30

Emulsion and Aqueous Solution Polymer Blends

A carboxylated acrylate emulsion copolymer was compounded with a polyacrylamide solution polymer to afford adhesive 5121-17. This adhesive displayed similar initial peel values, but lower peel values after heat aging on liner compared to the carboxylated acrylate emulsion adhesive 5042-184C.

35

An acrylamide acrylate emulsion copolymer was compounded with a polyacrylic acid ammonium salt solution to provide adhesive 5121-16. This adhesive displayed high initial peel values and similar applied heat aged peel values compared to the acrylamide acrylate emulsion copolymer adhesive 5042-184D. In this set of data, the use of the polyacrylic acid solution polymer was found to enhance the peel performance profile of an acrylamide acrylate emulsion copolymer

40

adhesive.

Interpenetrating Polymer Networks (IPN)

Two IPN systems were prepared. An acrylamide-containing IPN was
5 formed in a carboxylated acrylate emulsion polymer (4846-82 and 5121-48A,
respectively), and a carboxylated IPN was formed in an acrylamide-containing
acrylate emulsion polymer (4846-84 and 5121-48B, respectively). An increase in
mean particle size during the IPN reactions, conversion, and performance
similarities in alternate IPN first and second stage polymerization arrangements is
10 evidence for actual IPN formation.

Both IPN emulsion adhesives listed in Table 19 displayed very similar
adhesive performance, showing good initial peel and tack values, and low peel
build upon applied heat aging. Adhesive 4121-48B, an acrylic acid IPN, displayed
the best peel profile in these comparisons with 30 minutes dwell of 14 oz, 24 hour
15 dwell of 18 oz, one week dwell values of 19 oz, and one week dwell at elevated
temperature of 22 oz.

Comparison of adhesive properties obtained for the first stage emulsion
polymers (5121-18A and 5121-18B) demonstrated how significantly the
networking of alternate hydrophilic polymer functionality (*i.e.*, carboxylic acid and
20 amide) enhances the performance profile of these removable pressure sensitive
adhesives.

EXAMPLE 11

Amide-bearing monomers were evaluated at equivalent stoichiometries in
25 order to determine the effect of amide structure of polymer adhesive performance.
Copolymerizations of the preferred 5042-154 (4886-155) adhesive composition
containing 1.0 phm acrylamide were conducted with N-alkyl substituted
acrylamides and methacrylamides, N-phenylacrylamide, and N,N-
methylenebisacrylamide in place of the acrylamide. A copolymerization with
30 fumaramide (fumaric acid mono-amide) was attempted, but the monomer emulsion
formed a precipitate. A copolymerization with N-methylolacrylamide (1.42 phm)
afforded an unstable emulsion polymer that gelled at the end of the polymerization
reaction. These emulsion polymerizations are summarized in Table 20, below.

TABLE 20
Emulsion Polymerization^a Summary

Laboratory Reference	Amide Monomer	MW (g. mol ⁻¹)	Acrylamide Equivalent Weight	Polymer Composition ^b Amide/AA/Sty/BA	Final ^b Solids (wt-%)	Final ^c Viscosity (cps)	Final pH	Particle Size (nm)
5042-154	Acrylamide	71.08	1.00	1.00/2.00/4.50/92.50	58.9	1600	2.3	240
5121-54	Methacrylamide	85.11	1.20	1.20/2.00/4.50/92.30	59.5	1310	3.3	230
5121-56	N-Ethylacrylamide	99.13	1.39	1.39/2.00/4.50/92.11	58.7	890	1.9	240
5121-58	N-Octylacrylamide	183.29	2.58	2.58/2.00/4.50/90.92	59.5	500	2.0	250
5121-60	N-Methylmethacrylamide	99.13	1.39	1.39/2.00/4.50/92.11	59.8	410	2.1	290
5121-68	N-tert-Butylacrylamide	127.18	1.79	1.79/2.00/4.50/91.71	59.2	700	2.5	240
5121-70	N-tert-Butylmethacrylamide	141.21	1.99	1.99/2.00/4.50/91.51	58.6	900	2.4	220
5121-73	N-Methylolacrylamide	101.11	1.42	1.42/2.00/4.50/92.08	-----Emulsion Polymer Unstable----			
5121-75	N,N-Methylenebisacrylamide	154.17	1.08	1.08/2.00/4.50/92.42	59.0	550	2.1	240
5121-78	N-Phenylacrylamide	147.17	2.07	2.07/2.00/4.50/91.43	56.1	500	2.3	200
5121-80	Fumaramide	115.09	1.62	1.62/0.00/4.50/93.88	-----Monomer Emulsion Unstable----			

Footnotes to Table 20

- 5 a) All emulsion polymerizations were conducted in deionized water with pre-emulsified monomer in deionized water containing 9.0% (phm) Triton X-200 surfactant. Polymerizations were initiated with a sodium bisulfite postassium persulfate initiator system. Reactions were carried out at 80°C with delayed monomer emulsion and potassium persulfate solution additions over a three hour period. See 5042-154 as a standard example. Residual substituted amide monomers were all determined to be less than 0.1 wt-% in the final latex products (5121-54, 56, 58, 60, 68, 70, 75 and 10 78).
- b) AMD = Acrylamide
AA = Acrylic Acid
STY = Styrene
BA = n-Butyl Acrylate
15 Polymer composition in monomer weight percent.
Compounding was conducted with 2.0 wt-% (dry/dry polymer) Strodex SEK-50 phosphate surfactant and aqueous ammonia to produce coatable pressure sensitive adhesives. These compositions are summarized in Table 21, below.
- 20

TABLE 21
Compounding Summary
Amide Monomer Variations

Laboratory Reference	Base Latex Polymer Reference	Latex (g)	Latex Solids (wt-%)	D.I. Water (g)	Strodex SEK-50 ^a (g)	Final pH ^b	Final Solids ^c (wt-%)	Final Viscosity (cps)
5121-81A	5121-54	150	59.5	18	3.6	8.8	53.2	3030
5121-81B	5121-56	150	58.7	16	3.5	8.8	53.0	3200
5121-81C	5121-58	150	59.5	18	3.6	8.9	52.2	1600
5121-81D	5121-60	159	59.8	19	3.6	8.9	52.2	3300
5121-81E	5121-68	150	59.2	18	3.6	8.9	53.0	3200
5121-81F	5121-70	150	58.6	16	3.5	8.9	52.7	3450
5121-81G	5121-75	150	59.0	17	3.5	8.9	51.5	3400
5121-81H	5121-78	150	56.1	9	3.4	8.8	53.4	3300
5121-81I	5042-154	150	58.9	17	3.5	8.9	53.0	3500

Footnotes to Table 21

- a) 2.0 wt-% dry phosphate surfactant n dry emulsion polymer level.
- b) All emulsions were basified with 26° aqua ammonia and were self-thickening upon basification.
- 5 c) Non-volatile weight percent

Adhesive performance properties recorded are set forth in Table 22.

TABLE 22

Adhesive Performance^a Summary
Initial Film and (Aged Film)^b Properties
Amide Monomer Variations

Laboratory Reference	Polymer Architecture	Dwell Time			Loop Tack		Polyken Tack (g)	Shear 1" x 1/2" x 1 kg (hrs)
		30 min.	24 Hr.	Week	70°C	(lbs/in)		
5121-81A	Methacrylamide	4.2 (1.9)	4.5 (2.8)	6.2	14.6	0.8 (1.1)	280 (260)	21.3 PD (13.8 C)
5121-81B	N-Ethylacrylamide	6.8 (2.9)	7.2 (3.6)	7.2	18.2	1.1 (1.2)	330 (250)	4.8 C (5.8 C)
5121-81C	N-Octylacrylamide	8.5 (9.2)	11.9 (11.9)	18.8	31.2	1.5 (1.2)	380 (260)	1.6 C (1.8 C)
5121-81D	N-Methylmethacrylamide	4.0 (3.7)	5.2 (5.2)	10.4	20.5	1.0 (1.2)	320 (240)	3.6 C (1.6 C)
5121-81E	N-tert-Butylacrylamide	8.2 (6.6)	8.9 (11.5)	17.4	30.1	1.3 (1.2)	330 (260)	2.0 C (2.1 C)
5121-81F	N-tert-Butylmethacrylamide	7.6 (9.3)	12.9 (13.6)	22.1	31.8	1.5 (1.7)	510 (280)	1.2 C (1.3 C)
5121-81G	N-N-Methylenebisacrylamide	0.2 (0.5)	0.6 (0.6)	0.7	1.6	0.3 (0.4)	130 (110)	56.5 PD (0.1 A)
5121-81H	N-Phenylacrylamide	10.9 (11.2)	14.2 (16.0)	17.8	24.5	1.1 (1.4)	300 (310)	0.3 C (0.3 C)
5121-81I	Acrylamide	6.1 (5.2)	10.9 (8.3)	14.4	27.0	1.0 (0.9)	250 (260)	11.3 PD (110.0 C)

a) Adhesive evaluations were conducted with 1.0 ± 0.1 mil dry adhesive films transfer coated from H.P. Smith 8024 release liner to 2. mil polyester film. All testing was conducted off stainless steel

b) Heat aging was conducted at 70°C (158°F) in forced air ovens for one week. Data for films heat aged on liner prior to adhesive testing is in parentheses. All heat aged films and laminates were re-equilibrated to 72°F, 50% relative humidity for one day prior to testing.

All adhesives displayed clean removability after dwell periods of stainless steel.

N-Alkyl Acrylamides

- 5 The N-alkyl acrylamides exhibited adhesive peel performance profiles that distinguish N-ethylacrylamide with a superior removable performance. The N-ethylacrylamide copolymer exhibited negligible adhesive peel build at ambient temperature and much less peel build after elevated temperature aging compared to acrylamide and the higher N-alkyl substituted acrylamides, viz, N-octylacrylamide and N-tert -butylacrylamide.
- 10

Methacrylamides

- 15 The methacrylamides evaluated generally yielded lower peel values than the acrylamide copolymers. Methacrylamide and N-methylmethacrylamide exhibited lower initial and aged peel values. N-tert-butylmethacrylamide afforded copolymer performance similar to N-tert-butylacrylamide. The lower peel values for methacrylamides may indicate that steric hindrance in the polymer chain mobility is significant for these copolymers at the 1.0% phm level.

20 N-Aryl Acrylamides

An example of an aromatic N-substituent was evaluated with N-phenylacrylamide copolymerization. The resulting adhesive afforded a good removable peel profile from initial values (11 oz) to applied heat-aged peel (24 oz).

25 Poly-functional Acrylamides

- N,N-methylenebisacrylamide was employed as an example of a poly-functional monomer. In this case, both amide functionality and multiple polymerization sites for crosslinking reactions are present in the monomer. The resulting copolymer adhesive displayed very low initial peel values and applied aging peel values. This peel profile could have value as an ultra removable pressure sensitive adhesive that remains ultra removable after applied heat-aging cycles.
- 30

EXAMPLE 12

- 35 Variations of the preferred n-butyl acrylate emulsion polymerization (5042-154 or 4886-155) are summarized in Table 23, below.

AS SUBMITTED BY APPLICANT

TABLE 23
Emulsion Polymerization^a Summary

Laboratory Reference	Monomer Variation	pH ^m	Other Monomers VA/BA/STY/AA/AMDB ^q	Final ^c Solids (wt-%)	Final ^d Viscosity (cps)	Final pH	Particle ^e Size (nm)
5042-154	n-Butyl Acrylate	92.5	0.0/92.5/4.5/2.0/1.0	58.9	1600	2.3	240
5121-96	n-Butyl Acrylate ^e	92.5	0.0/92.5/4.5/2.0/1.0	60.2	1250	2.2	250
5121-98	Stearyl Methacrylate (Octadecyl Methacrylate)	30.0	0.0/62.5/4.5/2.0/1.0	51.0	30	2.1	150
5121-105	n-Butyl Vinyl Ether ^f	50.0	0.0/47.0/0.0/2.0/1.0	37.0 ^g	9270	2.1	180
5121-107	Diocetyl Maleate	50.0	0.0/47.0/0.0/2.0/1.0	57.2	1310	2.4	290
4864-88	Vinylidene Chloride	50.0	0.0/47.0/0.0/2.0/1.0	52.2	50	2.1	180
4864-90	Vinyl Versatates ^g (Vinyl Neodecanoate)	50.0	47.0/0.0/0.0/2.0/1.0	45.3	14	2.7	800
5121-116	Ethyl Acrylate	92.5	0.0/0.0/4.5/2.0/1.0	58.0	680	2.3	190
5121-118	Cyclohexyl Methacrylate	92.5	0.0/0.0/4.5/2.0/1.0	58.1	250	3.0	260
5121-128	Behenyl Methacrylate (Docosyl Methacrylate)	20.0	0.0/72.5/4.5/2.0/1.0	53.2	1670	2.0	230
5121-130	Stearyl Acrylate (octadecyl acrylate)	20.0	0.0/72.5/4.5/2.0/1.0	56.4	380	2.1	160
4987-182	2-Ethylhexyl Acrylate	45.0	0.0/47.5/4.5/2.0/1.0	57.6	910	2.9	340
5042-26	2-Ethylhexyl Acrylate	92.5	0.0/0.0/4.5/2.0/1.0	56.5	1550	2.6	560

Footnotes to Table 23

- 5 a) Experimental descriptions for these emulsion polymerizations can be found in laboratory notebooks C4864, 5042 and 5121. Emulsion polymerization 5042-154 is the standard reaction with 9.0 (phm) Triton X-200 surfactant upon which variations were made.
- 10 b) VA = Vinyl Acetate
BA = n-Butyl Acrylate
STY = Styrene
AA = Acrylic Acid
AMD = Acrylamide
Polymer composition in monomer weight percent.
- c) Brookfield RVF viscosity at 20 rpm, 25°C.
- d) Unimodal distribution means obtained on a Coulter Model N4 particle size analyzer.
- 15 e) Triton X-200, an anionic octyl phenol polyether sulfonate sodium salt polymerization surfactant, was replaced with IGEPAL CA 897, a nonionic ethoxylated octyl phenol surfactant
- f) Poor reactivity
- g) VV-10 vinyl monomer, Shell Chemical Co.

20 The n-butyl acrylate polymerization was conducted with anionic (Triton X-200) surfactant and nonionic (Igepal CA 897) surfactant. Acrylate esters were varied from ethyl acrylate C₅ monomer to stearyl acrylate C₂₁ monomer and behenyl methacrylate C₂₆ monomer. An example of a monomer containing cyclic aliphatic ester also was demonstrated with cyclohexyl methacrylate. Non-acrylate

25 monomers dioctyl maleate, vinylidene chloride, and vinyl versatate also were copolymerized. An emulsion polymerization with n-butyl vinyl ether afforded poor monomer conversion and , therefore, was not evaluated.

These emulsion polymerization variations were compounded with phosphate coester surfactant and basified with aqueous ammonia to afford pressure

30 sensitive adhesive modifications. Both tackified and untackified adhesives were evaluated. The formulations are summarized in Tables 24 and 25, below.

TABLE 24
Monomer Variations
Compounding Summary

Laboratory Reference	Base Latex Polymer Reference	Adhesives						Final pH	Final Viscosity (cps)
		Latex (g)	Latex Solids (wt-%)	D.I. Water (g)	Strodex SEK-50 ^a (g)	Colloid 679 (g)	Aqua Ammonia (g)		
5121-126A	5121-96	150	60.2	20.0	3.6	0.4	1.0	8.3	4040
5121-126B	5121-98	150	51.0	--	3.1	0.3	1.2	8.2	1960
5121-126C ^b	5121-105 ^b	150	37.0	--	2.2	0.2	1.6	8.0	960
5121-126D	5121-107	150	57.2	11.9	3.4	0.3	1.6	8.8	4850
5121-126E	4886-88	150	52.2	--	3.1	0.3	0.8	8.3	2620
5121-126F	4886-90	150	45.3	--	2.7	0.3	1.8	8.1	60
5121-126G	5121-116	150	58.0	--	3.5	0.4	1.4	8.5	4200
5121-126H	5121-118	150	58.1	--	3.5	0.4	1.5	8.9	50
5121-133A	5121-128	100	53.2	0.4	2.1	0.2	1.3	9.0	3100
5121-133B	5121-130	100	56.4	6.4	2.2	0.2	1.3	9.2	3340
5121-81I	5042-154	150	58.9	17.0	3.5	--	--	8.9	3500
C5042-28A	4987-182	82	~57.6	10.0	2.0	0.2	2.0	8.6	3045
C5042-28C	5042-26	82	~56.5	10.0	2.0	0.2	2.0	8.5	2800

a) 2.0 wt-% dry phosphate surfactant on dry emulsion polymer level.

b) Sample turned dark brown and separated into two layers.

TABLE 25
Monomer Variations
Compounding Summary
Tackified Adhesives

5	Laboratory	Compounded Adhesive	Compounded Adhesive	AQUATAC 6085
	Reference	Reference	(grams)	(grams)
	5121-126I	5121-126A	50	15
	5121-126J	5121-126B	50	15
	5121-126L	5121-126D	100	30
10	5121-126M	5121-126E	50	15
	5121-126N	5121-126F	50	15
	5121-126O	5121-126G	50	15
	5121-126P	5121-126H	50	15
	5121-133C	5121-133A	50	15
15	5121-133D	5121-133B	50	15

Adhesive performance results recorded are summarized in Table 26 for the untackified formulations and in Table 27 for the tackified formulations.

TABLE 26
Compounded Adhesive Performance^a Summary
Initial Film and (Aged Film)^b Properties
Monomer Variations

Laboratory Reference	Monomer Variation	Coating ^c	180° Peel (oz/in) Dwell Time		24 Hr. 70°C	Loop Tack (lbs/in)	Polyken Tack (g)	Shear 1" x 1/2" x 1 kg (hrs)
			30 min	24 Hr.				
5121-126A	n-Butyl Acrylate	I	2.7 L (3.2 L)	3.7 (4.4)	3.4 D	0.5 (0.4)	140 (220)	2.4 D
5121-126B	Stearyl Methacrylate	I	1.6 (0.8)	7.7 (2.3)	3.6	0.5 (0.1)	60 (30)	18.3 C
5121-126D	Diocetyl Maleate	D	0.0 G (0.0 G)	0.1 G (0.0 G)	0.1 G	0.2 (0.2 G)	240 (200)	0.0 C
5121-126E	Vinylidene Chloride	I	1.4 Z (3.4 Z)	32.4 (16.6)	37.0 Y	0.1 (0.1)	20 (0)	67.4 C
5121-126F	Vinyl Versatate/VA	D	0.0 D (0.5 D)	0.6 D (0.8 D)	2.4 Z	0.0 (0.0)	0 (0)	0.0 A
5121-126G	Ethyl Acrylate	D	0.1 (6.1)	0.8 (2.3)	14.3	0.1 (0.2)	30 (0)	4.6 A
5121-126H	Cyclohexyl Methacrylate	D	0.0 N (0.0 N)	0.0 N (0.0 N)	0.0	0.0 (0.0)	0 (0)	0.0 A
5121-133A	Behenyl Methacrylate	D	3.0 (2.0)	3.9 (5.4)	14.0 G	0.0 (0.2)	60 (80)	7.8 PD
5121-133B	Stearyl Acrylate	I	2.1 (1.0)	7.6 (2.4)	7.3	0.5 (0.3)	90 (120)	8.6 C
5121-81I	n-Butyl Acrylate	D	4.3 (2.8)	8.8 (6.3)	17.1	1.1 (0.8)	260 (290)	40.0 C
5121-81I	n-Butyl Acrylate	I	6.0 (4.1)	13.4 (8.2)	23.5	0.9 (1.0)	310 (290)	21.7 C
5042-34 ^e	n-Butyl Acrylate/2EH ^d	I	15(4)	20(10)	--	--	300 (220)	1.9 PD (0.4A)
5042-35 ^e	2-EHAd	I	18(10)	19(12)	--	--	350 (270)	0.4 PD (0.3 PD)

Footnotes to Table 26

- a) Adhesive evaluations were conducted with 1.0 ± 0.1 mil dry adhesive films transfer coated from H.P. Smith 8024 release liner to 2 mil polyester film. All testing was conducted off stainless steel
- 5 All adhesive failures are adhesive unless otherwise noted as follows: A = Adhesive, C = Cohesive, D = Delamination, N = Non-adhesive, G = Ghosting, Z = Zippering, Y = Yellowed.
- b) Heat aging was conducted at 70°C (158°F) in forced air ovens for one week. Data for films heat aged on liner prior to adhesive testing is in parenthesis. All heat aged films and laminates are re-equilibrated to 72°F, 50% relative humidity for one day prior to testing.
- 10 c) Adhesives that afforded coatings with metering rod drawdowns on H.P. Smith 8024 silicone release liner were transfer coated to polyester film and are designated I for indirect coating. Adhesives that did not coat the silicone release liner were directly coated on the polyester film and are designated D for direct coat.
- 15 d) 2-EHA is 2-ethylhexyl acrylate
- e) Transfer coated to 3.5 mil vinyl film rather than polyester film as with the other samples tested.

TABLE 27
Tackified Adhesive Performance^a Summary
Initial Film and (Aged Film)^b Properties

Laboratory Reference	Monomer Variation	Coating ^c	Monomer Variations					Loop Tack (lbs/in)	Polyken Tack (g)	Shear 1" x 1/2" x 1 kg (hrs)
			180° Peel (oz/in)		Dwell Time					
			30 min	24 Hr.	24 Hr	24 Hr 70°C				
5121-126I	n-Butyl Acrylate	I	13.7 L (16.1)	19.7 L (16.0)	26.5 D	1.7 (1.6)	390 (340)	2.9 PD		
5121-126J	Stearyl Methacrylate	I	16.7 (16.4)	28.9 (22.0)	40.0	0.8 (0.8)	90 (0)	6.4 C		
5121-126L	Dioctyl Maleate	D	1.6 G (2.0 G)	2.4 C (2.4 G)	2.9 C	0.9 G (0.8)	340 (340)	0.0 C		
5121-126M	Vinylidene Chloride	D	2.3 Z (1.8 Z)	5.2 D (3.0 Z)	7.4 D, Y	0.0 (0.0)	0 (0)	58.6 C		
5121-126N	Vinyl Versatate/VA	D	0.0 (0.0)	0.1 D (0.0)	9.0 D	0.0 (0.0)	0 (0)	0.0 A		
5121-126O	Ethyl Acrylate	D	0.6 G (0.2 Z)	0.4 G (0.4 Z)	1.0 G,Z	0.0 (0.0)	0 (0)	45.5C		
5121-126P	Cyclohexyl Methacrylate	D	0.0 (0.0)	0.0 (0.0)	0.0	0.0 (0.0)	0 (0)	0.0 A		
5121-133C	Behenyl Methacrylate	D	12.2 (8.2)	13.1 L (25.3)	33.7	0.5 (1.0)	130 (80)	4.1 C		
5121-133D	Stearyl Acrylate	D	16.0 (10.0)	27.2 (27.2)	38.0	0.8 (0.8)	250 (100)	2.7 C		

Footnotes to Table 27

- a) Adhesive evaluations were conducted with 1.0 ± 0.1 mil dry adhesive films transfer coated from H.P. Smith 8024 release liner to 2 mil polyester film. All testing was conducted off stainless steel
- 5 All adhesive failures are adhesive unless otherwise noted as follows: A = Adhesive, C = Cohesive, D = Delamination, N = Non-adhesive, G = Ghosting, Z = Zippering, Y = Yellowed.
- b) Heat aging was conducted at 70°C (158°F) in forced air ovens for one week. Data for films heat aged on liner prior to adhesive testing is in parenthesis. All heat aged films and laminates are re-equilibrated to 72°F, 50% relative humidity for one day prior to testing.
- 10 c) Adhesives that afforded coatings with metering rod drawdowns on H.P. Smith 8024 silicone release liner were transfer coated to polyester film and are designated I for indirect coating. Adhesives that did not coat the silicone release liner were directly coated on the polyester film and are designated D for direct coat.
- 15

Emulsion Polymerization Surfactant

- Adhesive results obtained for the n-butyl acrylate emulsion polymer prepared
- 20 with the nonionic surfactant (5121-126A) indicate substitution of the anionic surfactant (Triton X-200) with a nonionic surfactant (Igepal CA 897) detracted from the adhesive performance as noted by delamination after applied heat aging.

Higher and Lower Acrylate Polymer Variations

- 25 Pressure sensitive adhesives were prepared with acrylate and methacrylate esters ranging from ethyl acrylate C₅ to behenyl methacrylate C₂₆. These results are indicative that n-butyl and 2-ethylhexyl acrylate esters exhibit the most utility in the preparation of high performance removable pressure sensitive adhesives.

- Higher acrylate esters may have use for modification of performance. For
- 30 example, the stearyl acrylate adhesive (5121-133B) exhibited no peel build upon applied aging in this testing.

Non-Acrylate Polymer Variations

- All non-acrylate monomer substitutions in this study afforded poorer
- 35 adhesive performance. The dioctyl maleate and vinyl versatate copolymers were too hard for typical pressure sensitive applications.

- The vinylidene chloride/n-butyl acrylate copolymer adhesive (5121-126E) displayed an interesting peel profile that could have some utility for a repositionable adhesive. Although the adhesive discolored, it removed cleanly after applied heat
- 40 aging.

EXAMPLE 13

- Adhesives formulations based on copolymer emulsion 4886-155, viz, with
- 5 Strodex SEK-50 surfactant (see Table 9, Example 6) were compounded with aqueous ammonia, lithium hydroxide, and sodium hydroxide aqueous solutions. Adhesive performance evaluation included transfer coating the adhesive to polyester face stock and testing off of stainless steel, as described above. The results recorded are displayed in Table 28 below.

TABLE 28
Base Effects on Adhesive Performance

Laboratory Reference	Base	180° Peel (oz/in)					
		30 min. 72°F	24 Hr. 72°F	Week 72°F	Month 72°F	24 Hr. 158°F	Week 158°F
AROSET 1185 #0094DC	NH ₃	2.5*	6.7	13.2	29.1	23.2	31.2
5121-127	LiOH	2.4	7.8	20.9	40.8	19.2	12.8
5121-100	NaOH	2.8	3.1	5.2	20.3	7.6	7.2
C5121-135, 143							

*This average value is lower than the typical 8 oz. peel values obtained in previous measurements.

These results demonstrate that the choice of basification agent influences peel performance. Lithium hydroxide afforded higher peels than ammoniation after extended room temperature applied aging. Sodium hydroxide offered lower peels than ammoniation after extended room temperature and 158°F applied aging. Both alkali metal salts exhibited large differences between room temperature applied aging and heat aging at 158° F.

EXAMPLE 14

10

Adhesive formulations 4987-77 (copolymer emulsion 4886-155 of Example 1, Strodex SEK-50 surfactant, and aqueous ammonia, see Table 9, Example 6), and 4987-78 (copolymer emulsion 4886-155, Gafac RD-510 surfactant, and aqueous ammonia, see Table 9, Example 6), were coated on super calendered kraft paper release liner at 1.0 and 0.6 mil dry thickness. Label face stocks included unprimed 50 lb semi-gloss litho paper, 2 mil polyester, 3.5 mil vinyl, and a coated thermal paper. These coated label stocks were evaluated on a variety of plastic (*i.e.*, polyethylene, polypropylene, polystyrene, polyacrylate, ABS, PVC, and polycarbonate), metal (*i.e.*, aluminum and stainless steel), and glass substrates.

20

The plastic substrates possess different surface energies ranging from relative low values for polyolefins to higher values for engineering plastics such as polyvinyl chloride (PVC) and polycarbonate. High performance removable characteristics for an adhesive are determined, in part, by the ability of the adhesive to anchor well to a low surface energy polyolefin surface and also remove cleanly from high surface energy plastics like polycarbonate.

25

The results of this series of tests are displayed in the following tables.

TABLE 29
Applied Peel Adhesion (lbs/in)
4987-77

Label Face Stick	PE	PP	PS	PA	ABS	PVC	PC	GLASS	AL	SS
<u>Polyester</u>										
30 min @ 72°F	0.1	0.1	1.3	1.6	1.6	2.3	2.0	0.3	0.5	0.6
24 hr @ 72°F	0.1	0.1	2.1	2.6	2.7	3.0	3.0	0.2	0.1	0.3
1 week @ 72°F	0.1	0.1	2.7	3.1	3.0	2.8	3.0	0.6	0.1	0.3
1 week @ 158°F	0.2	0.2	2.3	1.8	2.7	2.9	2.3	0.7	0.2	1.3
3 weeks @ 158°F	0.1	0.4	2.7	2.3	3.5	3.1	2.7 L	0.7	0.1	1.7
<u>Vinyl</u>										
30 min @ 72°F	0.1	0.3	2.0	2.3	2.1	3.0	2.8	0.5	0.6	1.3
24 hrs @ 72°F	0.1	0.4	2.8	3.2	3.1	3.5	3.8	0.9	0.3	1.0
1 week @ 72°F	0.2	0.6	3.7	3.9	3.8	3.7	3.7	1.0	0.2	0.7
1 week @ 158°F	0.2	0.3	2.9	2.2	3.1	3.3	2.9	1.3	0.7	0.4
3 weeks @ 158°F	0.1	0.2	2.4	1.1	2.6	3.5	3.0	0.3	0.1	0.4

Coating Parameter: 1.0 mil Dry

L = Legging D = Delamination G = Ghosting S = Split PT = Paper Tear

TABLE 30
Applied Peel Adhesion (lbs/in)
4987-78

Label Face Stick	PE	PP	PS	PA	ABS	PVC	PC	GLASS	AL	SS
<u>Polyester</u>										
30 min @ 72°F	0.0	0.1	1.1	1.4	1.2	1.0	1.4	0.1	0.2	0.5
24 hr @ 72°F	0.0	0.0	1.6	2.3	2.0	2.5	2.5	0.0	0.0	0.1
1 week @ 72°F	0.0	0.0	2.6	2.9	2.5	3.1	2.8	0.3	0.0	0.0
1 week @ 158°F	0.1	0.2	2.6	2.3	2.5 L	3.0	3.6 D	0.0	0.0	0.2
3 weeks @ 158°F	0.1	0.3	2.8	2.9	3.7	3.9 D	2.8 L	1.4	0.0	1.2
<u>Vinyl</u>										
30 min @ 72°F	0.0	0.1	1.7	2.3	1.8	2.2	2.3	0.1	0.3	0.6
24 hrs @ 72°F	0.0	0.1	2.3	3.2	3.0	3.4	3.3	0.0	0.0	0.1
1 week @ 72°F	0.0	0.1	3.0	4.0	3.4	3.3	3.5	0.2	0.0	0.1
1 week @ 158°F	0.2	0.2	2.3	1.7	2.5	3.3	1.5 L	0.2	0.0	0.8
3 weeks @ 158°F	0.1	0.1	1.8	1.0	2.1	3.9	2.1	0.2	0.0	0.9

Coating Parameter: 1.0 mil Dry

L = Legging D = Delamination G = Ghosting S = Split PT = Paper Tear

TABLE 31
Film Aging

	Peel Adhesion (lbs/in)						Polyken Tack (g)				Shear	
	30 min. Dwell			24 hr. Dwell							1" x 1/2" x 1 kg (hrs)	
	Mylar	Vinyl	Paper	Mylar	Vinyl	Paper	Mylar	Vinyl	Paper	Mylar	Vinyl	Paper
<u>4987-77</u>												
2 wk, RT	0.6	1.3	PT	0.3	1.0	PT	260	160	240	12.4S	24.9S	22.5S
1 wk, 158°F	0.1	0.1	1.3	0.3	0.1	1.6	320	140	330	2.3A	0.0A	1.9A
3 wk, 158°F	0.3	0.0	1.6	0.4	0.0	2.3	185	100	300	2.3A	0.0A	0.8A
<u>4987-78</u>												
2 wk, RT	0.5	0.6	1.4	0.1	0.1	0.4	230	200	240	1.1A	3.6A	4.8A
1 wk, 158°F	0.1	0.1	0.8	0.0	0.1	0.2	270	150	250	2.3A	0.0A	3.4A
3 wk, 158°F	0.1	0.0	1.3	0.0	0.0	1.3	210	90	250	0.5A	0.0A	0.2A

Coating Parameter: 1.0 mil dry film

L = Legging D = Delamination G = Ghosting S = Split PT = Paper Tear

TABLE 32

Applied Peel Adhesion (lbs/in)

50 lb Paper

Label Face Stick	PE	PP	PS	PA	ABS	PVC	PC	GLASS	AL	SS
<u>4987-77</u>										
30 min @ 72°F	0.5	1.4	PT	PT	PT	PT	PT	1.5	PT	PT
24 hr @ 72°F	0.7	1.4	PT	PT	PT	PT	PT	1.4	1.2	PT
1 week @ 72°F	0.9	1.4	PT	PT	PT	PT	PT	2.1	1.0	PT
1 week @ 158°F	1.0	0.7	PT	PT	PT	PT	PT	3.6	1.0	PT
3 weeks @ 158°F	0.9	1.4	PT	PT	PT	PT	PT	PT	1.3	PT
<u>4987-78</u>										
30 min @ 72°F	0.2	0.7	PT	PT	PT	PT	PT	1.2	PT	1.4
24 hrs @ 72°F	0.4	0.8	PT	PT	PT	PT	PT	0.1	0.2	0.4
1 week @ 72°F	0.7	0.7	PT	PT	PT	PT	PT	1.5	0.2	0.4
1 week @ 158°F	0.7	0.7	PT	PT	PT	PT	PT	1.5	0.2	0.4
3 weeks @ 158°F	0.9	1.3	PT	PT	PT	PT	PT	1.4	0.1	PT

Coating Parameter: 1.0 mil Dry

L = Legging D = Delamination G = Ghosting S = Split PT = Paper Tear

TABLE 33

Film Aging
50 lb Paper

	Peel Adhesion (lbs/in)		Polyken Tack (g)	Shear 1" x 1/2" x 1 kg (hrs)
	30 min. Dwell Paper	24 hr. Dwell Paper		
<u>4987-77</u>				
2 wk, RT	PT	PT	240	22.5S
1 wk, 158°F	1.3	1.6	330	1.9A
3 wk, 158°F	1.6	2.3	300	0.8A
<u>4987-78</u>				
2 wk, RT	1.4	0.4	240	4.8A
1 wk, 158°F	0.8	0.2	250	3.4A
3 wk, 158°F	1.3	1.3	250	0.2A

Coating Parameter: 1.0 mil dry film

L = Legging D = Delamination G = Ghosting S = Split PT = Paper Tear

TABLE 34
Film Aging
50 lb Paper

	Peel Adhesion (lbs/in)		Polyken Tack (g) Paper	Shear 1" x 1/2" x 1 kg (hrs) Paper
	30 min. Dwell Paper	24 hr. Dwell Paper		
<u>4987-77</u>				
2 wk, RT	1.2	PT	140	10.5C
1 wk, 158°F	1.1	1.6	220	
3 wk, 158°F	1.5	PT	210	0.8A
<u>4987-78</u>				
2 wk, RT	0.5	0.3	160	3.3A
1 wk, 158°F	0.5	0.8	190	
3 wk, 158°F	1.2	0.8	160	0.6A

Coating Parameter: 0.6 mil dry film

L = Legging D = Delamination G = Ghosting S = Split PT = Paper Tear

TABLE 35

Thermal Paper Application (1.0 Mil)
Adhesive Performance Off Stainless Steel

		<u>4987-77</u>	<u>4987-78</u>
5	<u>Applied Aging Properties</u>		
	180° Peel Adhesion (lb/in)		
	30 min. @ 72°F	2.7	0.5
	24 hr @ 72°F	2.4	0.2
	1 week @ 72°F	2.9	0.3
10	1 week @ 158°F	PT	1.3
	3 week @ 158°F	4.3	1.5
	<u>Unapplied Aging Properties</u>		
	180° Peel Adhesion (lb/in)		
	30 min. @ 72°F		
15	Initial	2.7	0.5
	1 week @ 158°F	0.8	0.8
	3 week @ 158°F	2.6	0.2
	Quick Tack (g)		
	Initial	370	290
20	1 week @ 158°F	280	280
	3 week @ 158°F	320	310
	Shear Resistance (hrs) (1" x 1" x kg)		
	Initial	>100	>100
25	1 week @ 158°F	--	
	3 week @ 158°F	>100	6 G

L = Legging D = Delamination G = Ghosting S = Split PT = Paper Tear

Applied Peel Adhesions After Aging--Tables 29-30

Adhesive 4987-77 displayed clean removability from all surfaces with excellent anchorage to polyester and vinyl film face stocks. Peel values vary from 0.1 lbs/in for polyethylene to over 3 lbs/in for higher surface energy plastics, *e.g.*

5 PVC.

Adhesive 4987-78 displayed lower peel values than did adhesive C4987-77 with values ranging from about 1 oz/in on polyethylene to about 3 lbs/in from higher surface energy plastics. Face stock anchorage was found to be very good with only two delaminations noted from PVC and polycarbonate substrates after applied heat

10 aging cycles.

Unapplied Adhesive Aging Characteristics--Table 31

Heat aging of laminated film face stock on liner was conducted in order to compare adhesive aging characteristics and vinyl plasticizer migration effects. Aged

15 vinyl films all showed loss of peel adhesion and Polyken tack compared to aged polyester films samples, which loss is attributed to plasticizer migration.

Paper Face Stock Evaluation--Tables 32-35

All adhesives exhibited paper tear on higher surface energy plastics.

20 Adhesive 4987-78 demonstrated the best paper face stock performance based on the data in Table 33 as noted by the polypropylene, glass, aluminum, and stainless steel comparisons.

Unapplied label stock aging results displayed in Tables 33 and 34 indicate that adhesive 4987-78 demonstrated the best paper face stock performance,

25 affording relatively stable adhesive performance and clean removability from stainless steel.

The data displayed at Table 35 shows that adhesive 4987-78 afforded excellent removability after both initial and applied heat aging off stainless steel.

I claim:

- 1 An aqueous pressure sensitive adhesive composition comprising in
water:
 - (a) a copolymer of a C₄-C₁₈ alkyl (meth)acrylate monomer and
between about 0.1 wt-% and 5 wt-% N-substituted or unsubstituted (poly)amide of
5 (meth)acrylic acid;
 - (b) a copolymer of a C₄-C₁₈ alkyl (meth)acrylate monomer and
about 0.2 wt-% and 10 wt-% of an ethylenically unsaturated carboxylic acid; and
 - (c) a surfactant,the weight ratio of amide to acid ranging from about 1:10 to 10:1, and said
10 copolymers (a) and (b) selected from:
 - (i) a blend of copolymers (a) and (b), at least one of
which is an emulsion copolymer,
 - (ii) an interpolmer of copolymers (a) and (b) where said
monomer of copolymers (a) and (b) are the same; and
 - 15 (iii) an interpenetrating polymer network emulsion of
copolymers (a) and (b).
2. The adhesive composition of claim 1 wherein said monomer of one
or more of said copolymers (a) and (b) is a C₄-C₁₂ alkyl (meth)acrylate monomer.
3. The adhesive composition of claim 2 wherein said monomer is
selected from the group consisting of n-butyl acrylate, 2-ethylhexyl acrylate, and
mixtures thereof.
4. The adhesive composition of claim 1 wherein said ethylenically
unsaturated carboxylic acid of said copolymer (b) is selected from the group
consisting of an acrylic or lower alkyl-substituted acrylic acid, crotonic acid,
isocrotonic acid, vinyl acetic acid, fumaric acid, maleic acid, glutaconic acid, allyl
5 malonic acid, allyl succinic acid, itaconic acid, and mixtures thereof.
5. The adhesive composition of claim 4 wherein said ethylenically
unsaturated carboxylic acid is acrylic acid.
6. The adhesive composition of claim 1 wherein one or more of said
copolymers (a) and (b) additionally contains up to about 25% by weight of one or
more of a styrene monomer, vinyl chloride, vinylidene chloride, or ethylene vinyl
acetate.

7. The adhesive composition of claim 6 wherein said styrene monomer is styrene or a lower-alkyl substituted styrene.

8. The adhesive composition of claim 6 wherein one or more of said copolymers (a) and (b) contains about 5% by weight of styrene.

9. The adhesive composition of claim 1 wherein said acrylamide:acid weight ratio is about 1:2.

10. The adhesive composition of claim 9 wherein said alkyl (meth)acrylate monomer is butyl acrylate or 2-ethylhexyl acrylate; and said unsaturated carboxylic acid is acrylic acid.

11. The adhesive composition of claim 1 which has been basified with a base.

12. The adhesive composition of claim 11 wherein said basification of said adhesive composition with a base is to a pH of between about 8 and 9.

13. The adhesive composition of claim 11 wherein said base is selected from the group consisting of aqueous ammonia, an amine, an imine, an alkali metal or alkaline earth metal hydroxide or carbonate.

14. The adhesive composition of claim 1 wherein said surfactant (c) is a phosphate ester surfactant.

15. The adhesive composition of claim 14 wherein said phosphate ester surfactant is selected from the group consisting of potassium alkyl aryl polyethoxy phosphate, potassium alkyl ethoxy phosphate, potassium alkyl phosphate, potassium alkyl polyethoxy phosphate, and mixtures thereof.

16. The adhesive composition of claim 1 wherein said copolymers (a) and (b) contain not more than about 15 wt-% of a cross-linking additive, cross-linking monomer, N-substituted acrylamide, a copolymerizable emulsifier, and zwitterionic monomer.

17. The adhesive composition of claim 1 wherein said emulsion

copolymer is synthesized to a non-volatile solids content of between about 50% and 65%.

18. The adhesive composition of claim 1 wherein residual unreacted monomer is removed from said copolymers (a) and (b) prior to forming said adhesive composition.

19. The adhesive composition of claim 1 wherein said copolymers (a) and (b) are synthesized under emulsion copolymer conditions including a pH of less than 4.

20. The dried residue of the adhesive composition of claim 1 coated on a film face stock or a release sheet.

21. The coated film face stock of claim 20 wherein said film face stock is formed from polymeric film, a cellulosic film, or metal film.

22. The dried residue of the adhesive composition of claim 10 coated on a film face stock.

23. A method for forming an aqueous emulsion acrylic pressure sensitive adhesive composition which comprises blending:

(a) a copolymer of a C₄-C₁₈ alkyl (meth)acrylate monomer and between about 0.1 wt-% and 5 wt-% N-substituted or unsubstituted (poly)amide of (meth)acrylic acid;

(b) a copolymer of a C₄-C₁₈ alkyl (meth)acrylate monomer and about 0.2 wt-% and 10 wt-% of an ethylenically unsaturated carboxylic acid; and

(c) a surfactant,

the weight ratio of amide to acid ranging from about 1:10 to 10:1, and said copolymers (a) and (b) selected from:

- (i) a blend of copolymers (a) and (b), at least one of which is an emulsion copolymer;
- (ii) an interpolymer of copolymers (a) and (b) where said monomer of copolymers (a) and (b) are the same; and
- (iii) an interpenetrating polymer network emulsion of copolymers (a) and (b).

24. The process of claim 23 wherein said blend is basified with a base.
25. The process of claim 24 wherein said base is selected from the group consisting of aqueous ammonia, an amine, an imine, an alkali metal or alkaline earth metal hydroxide or carbonate.
26. The process of claim 23 wherein said acrylic monomer is selected from the group consisting of n-butyl acrylate and 2-ethylhexylacrylate; said ethylenically unsaturated carboxylic acid is acrylic acid; one or more of said copolymers (a) or (b) additionally contains up to about 25 wt-% of styrene.
27. The process of claim 26 wherein one or more of said copolymers (a) or (b) contains about 5% styrene and said weight ratio of acrylamide to acrylic acid is about 1:2.
28. The process of claim 23 wherein said surfactant is a phosphate ester surfactant selected from the group consisting of salts of alkyl aryl polyethoxy phosphates, alkyl ethoxy phosphates, alkyl phosphates, alkyl polyethoxy phosphates, and mixtures thereof.
29. The process of claim 28 wherein said salts are of an alkali metal or ammonium.
30. The process of claim 23 wherein said emulsion copolymer is devoid of cross-linking additive, cross-linking monomer, N-substituted acrylamide, a copolymerizable emulsifier, and zwitterionic monomer.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/03750

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ¹ <small>According to International Patent Classification (IPC) or to both National Classification and IPC</small> IPC (5): B32B 7/12, 15/08; C08K 5/521; C09J 125/14, 133/02, 133/08, 133/10 133/26														
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched ²</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; text-align: left; border-bottom: 1px solid black;">Classification System ³</th> <th style="width: 70%; text-align: left; border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="padding: 5px;">U.S.</td> <td style="padding: 5px;">482/343, 344, 355; 523/201; 524/141, 145, 521, 533, 555 525/902, 903</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ³</div>			Classification System ³	Classification Symbols	U.S.	482/343, 344, 355; 523/201; 524/141, 145, 521, 533, 555 525/902, 903								
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; text-align: left; border-bottom: 1px solid black;">Category ⁵</th> <th style="width: 70%; text-align: left; border-bottom: 1px solid black;">Citation of Document, ¹⁴ with indication, where appropriate, of the relevant passages ¹⁵</th> <th style="width: 20%; text-align: left; border-bottom: 1px solid black;">Relevant to Claim No. ¹⁶</th> </tr> <tr> <td style="vertical-align: top; padding: 5px;">X, P</td> <td style="padding: 5px;">US, A, 4,983,656 (ITO ET AL.) 08 JANUARY 1991 See column 3, lines 6-20, column 3, line 64 to column 4, line 17; column 5, lines 15-45 and column 6, lines 64-68.</td> <td style="vertical-align: top; text-align: center; padding: 5px;">1-30</td> </tr> <tr> <td style="vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">US, A, 4,540,739 (MIDGLEY) 10 SEPTEMBER 1985 See column 2, line 61 to column 3, line 49, column 6, lines 32-43 and column 7, lines 33-38.</td> <td style="vertical-align: top; text-align: center; padding: 5px;">1-30</td> </tr> <tr> <td style="vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 4,351,875 (ARKENS) 28 SEPTEMBER 1982 See entire document.</td> <td style="vertical-align: top; text-align: center; padding: 5px;">1-30</td> </tr> </table>			Category ⁵	Citation of Document, ¹⁴ with indication, where appropriate, of the relevant passages ¹⁵	Relevant to Claim No. ¹⁶	X, P	US, A, 4,983,656 (ITO ET AL.) 08 JANUARY 1991 See column 3, lines 6-20, column 3, line 64 to column 4, line 17; column 5, lines 15-45 and column 6, lines 64-68.	1-30	X	US, A, 4,540,739 (MIDGLEY) 10 SEPTEMBER 1985 See column 2, line 61 to column 3, line 49, column 6, lines 32-43 and column 7, lines 33-38.	1-30	A	US, A, 4,351,875 (ARKENS) 28 SEPTEMBER 1982 See entire document.	1-30
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹³</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>														
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> Date of the Actual Completion of the International Search ⁸ <div style="text-align: center; padding: 5px;">13 AUGUST 1991</div> </td> <td style="width: 50%; vertical-align: top; padding: 5px;"> Date of Mailing of this International Search Report ⁹ <div style="text-align: center; padding: 5px;">18 SEP 1991</div> </td> </tr> <tr> <td style="vertical-align: top; padding: 5px;"> International Searching Authority ¹ <div style="text-align: center; padding: 5px;">ISA/US</div> </td> <td style="vertical-align: top; padding: 5px;"> Signature of Authorized Officer ¹⁰ <div style="text-align: center; padding: 5px;"> Joseph L. Schofer </div> </td> </tr> </table>			Date of the Actual Completion of the International Search ⁸ <div style="text-align: center; padding: 5px;">13 AUGUST 1991</div>	Date of Mailing of this International Search Report ⁹ <div style="text-align: center; padding: 5px;">18 SEP 1991</div>	International Searching Authority ¹ <div style="text-align: center; padding: 5px;">ISA/US</div>	Signature of Authorized Officer ¹⁰ <div style="text-align: center; padding: 5px;"> Joseph L. Schofer </div>								
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Continuation to FORM PCT/ISA/210 (second sheet).

I. CLASSIFICATION OF SUBJECT MATTER:

U.S. Cl: 428/343, 344, 355; 523/201; 524/141, 145, 521, 533, 555